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STUDIES IN GLAZES.

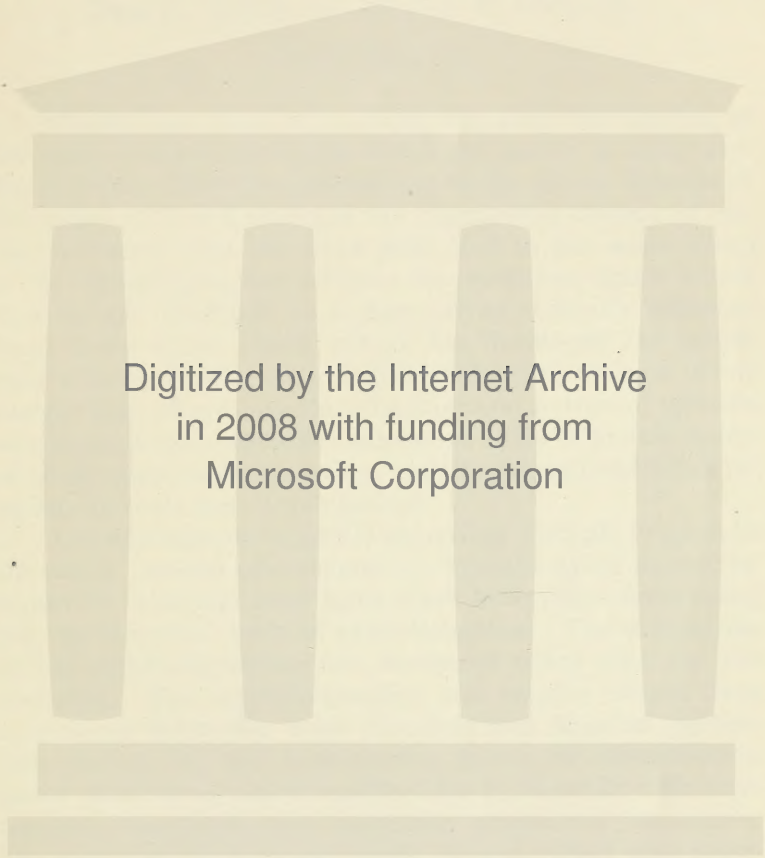
PART II.

CRYSTALLINE GLAZES.

BY

R. C. PURDY AND J. F. KREHBIEL.

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CRYSTALLINE GLAZES.

BY

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Champaign, Ill.

Crystalline glazes are among the most fascinating of the many ceramic problems which the potter is today trying to solve. They are fascinating to the artist, because of the many perfect forms and the unexpected display of colors produced from the same glaze and in the same burn; to the crystallographer, because the conditions under which crystals are developed in a glaze are so radically different from those under which nature has developed the larger part of her crystals; to the physical chemist, because of the insight they afford into the structure and nature of igneous solutions; to the ceramist because so little is known today of their range in composition, and the firing conditions requisite to their best development.

Crystallographers find it exceeding difficult to explain the many curious phenomena of crystallization occurring in nature, although they have much knowledge concerning the fundamental facts of crystallization. The difficulties of the crystallographer are increased many fold for the ceramist. The crystallographer can readily obtain type specimens, determine their chemical and physical properties, and in the end formulate a system of classification based upon them which enables him to identify with comparative readiness any inorganic crystalline substance. The ceramist, on the other hand, cannot collect type specimens of the crystals he produces, nor has he been able as yet to ascertain the conditions most suitable for their production. The ceramist's problem is further complicated by the fact that the production of crystals is in truth but a minor consideration in the manufacture of salable ware,

for above all things there must be maintained perfect physical harmony between the glaze and the body.

Strange as it may seem, it is a fact that the ceramist can profit but very little, except for methods of study, by the mineralogist's experience. Stull[1] has shown the futility of attempting to produce in a glaze matrix a condition that, theoretically considered, would cause the separation of material having the form and composition of some of nature's crystals. The fact of the case is, the ceramist has to deal with a set of conditions that require for their full understanding the establishment of physical and chemical laws which pertain to his special case. In the end, the science of producing crystals in glazes must be reduced to the same exactness as the science of metallurgy has been in the case of iron and steel, through the help of metallography.

It is indeed a long road to a full understanding of even a few of the simplest and most fundamental phenomena in a new field. Empirical researches must be many before very much progress can be made toward the discovery of laws underlying physico-chemical phenomena. We have a few desultory researches in crystalline glazes, very scattered records of successful attempts in their production, but a resume of these several researches is today productive of nothing short of confusion of ideas. Published records of systematic empirical studies must precede attempts to formulate laws or deduce facts. It was with these considerations in mind that the studies here reported were undertaken. No attempt has been made to deduce definite laws from the results of these experiments, but contentment is found in observing and recording the facts, so that some day, after more of the field has been surveyed, we can correlate the results and deduce laws that will place the production of crystalline glazes beyond the realm of chance and freak.

[1]Trans. Am. Cer. Soc., Vol. VI. p. 188

TYPE OF CRYSTALLINE GLAZES STUDIED.

Crystals have been produced in glazes having a wide variety of compositions, and at nearly all temperatures. It would be aside from the purpose of this paper to review all the types of glazes which have been reported as "crystalline," except for the sake of establishing the fact that there may be a wide variation in their composition and heat treatment, and to demonstrate that in a thorough study, such as is indicated in the title, it would be impossible to deal with more than one type. The following formulæ are sufficient for these purposes:

RIDDLE'S CRYSTALLINE GLAZE.[1]

0.700	ZnO			1.375	SiO_2
0.075	K_2O	0 0	Al_2O_3		
0.075	Na_2O				
0.150	CaO			0.225	B_2O_3

CONE 2 GLAZE.[2]

0.105	K_2O			1.805	SiO_2
0.189	Na_2O				
0.052	BaO	0.045	Al_2O_3		
0.029	CaO				
0.625	ZnO			0.378	B_2O_3

After reviewing the published records of many experiments, it was decided to limit the present studies to a type of glaze that is now popular in France, and which has been successfully used in this country to some extent; that is, a simple alkali-alkaline-earth silicate, in which the crystalline effect is produced by some simple crystallizers, the whole designed to mature at cone 10. The types of the glazes studied are given in the table at top of page 8.

[1]Trans. Am. Cer. Soc., Vol. VIII, p. 347.
[2]Sprechsaal, 1903.

TABLE I.

Crystalline Glaze Formulae.

Name	K_2O	ZnO	TiO_2	SiO_2	Ox.Ratio
Bries glaze No. 1	.300	.700	....	2.000	4.000
Bries glaze No. 2	.300	.700	.300	1.700	4.000
Heath's glaze	.300	.700	.500	2.000	5.000
Sevres glaze No. 1	.333	.666	....	2.000	4.000
Sevres glaze No. 2	.166	.833	....	1.94	3.870
Sevres glaze No. 3	.333	.666	.341	1.666	4.016
Sevres blend A { 85% No. 1 / 15% No. 2 }	.308	.691	....	1.991	3.983
Sevres blend B { 85% No. 3 / 15% No. 2 }	.308	691	.290	1.709	3.998
Stull's glaze, according to Gates..	.305	.695	.297	1.690	3.970

SCOPE OF INVESTIGATION.

Before attempting to outline a series of studies on fritted glazes, it is essential to consider the conditions that must prevail, in order to have a crystallizing compound separating out from a molten matrix. It is especially essential that we should understand the fundamental difference between a clear non-crystalline glaze, and a glaze in which clusters of crystals appear throughout the whole mass.

Primarily a glaze may be considered as a glass. Window glass, for instance, is a perfectly transparent and homogeneous compound. It has been proven beyond a doubt, however, that window glass has a tendency to crystallize. Crystals of wollastonite have been developed in one instance, and crystals of quartz in another, showing that even in so simple a compound as glass, consisting in the main of calcium oxide, soda, potash, silica and in some cases lead, there is what may be styled latent crystallization. Curious indeed is the fact that the potter has learned by empirical trials that the best crystalline effects are produced in a glassy matrix, which in composition is very much like the

mixture which the glass manufacturer has learned also by similar empirical trials will produce the best glass.

The belief that ordinary glass has a tendency to crystallize is strongly supported by the following quotation:

[1]"If one considers that the contents of silica in commercial glass is very variable, and that a higher temperature more of this acid can be taken up than can be retained by the glass as this temperature falls; that further, feldspathic minerals may be taken up and again separated by a molten glass; finally, also sulphates, phosphates, borates, metallic oxides may enter into the constitution of glass, it would appear that these facts allow of no other explanation than that commercial glasses are quickly solidified solutions, not only of different silicates in each other, but even solutions of basic oxides or silica and other salts and metals, in molten silicates. Whether in all glasses some fundamental silicates, a compound say of Na_2O, CaO, SiO_2, or Na_2O, CaO, 4 SiO_2, are to be taken as the solvent or not, must remain a question so long as nothing more definite is known than at present, yet many of the observations appear to speak for such an assumption."

Or the following:[2]

"A devitrified glass is a heterogeneous mixture, and while support is lent to the theory that the original undevitrified material is likewise a mixture, it cannot be accepted as conclusive proof. One cannot conceive the formation of such a heterogeneous mixture when a glass is devitrified by being kept for a long time at a high temperature, on the assumption that one is dealing with a mixture, more or less homogeneous, and that an agglomeration or segregation of the constituents takes place, giving rise to crystalline forms. But on the other hand, it is also conceivable that there is a real solution, as described by Benrath, supersaturated at a high temperature with some definite silicate or other compound which gradually crystallizes out. Hence the facts of devitrification may lend support to either theory."

Seydholt, Jackson and Rich, and others have etched glass with concentrated hydrofluoric acid, developing on the common sheet glass, crystals that are of various forms, some "star shaped," some as "rods with crystalline radiation on both sides," and in the lead glasses, "superposed rings" that certainly cannot be due to accidental irregularities in texture of the glasses.

[1]Benrath—"Die Glasfabrikation," Jour. Soc. of Chem., Ind., 1901.
[2]Jour. Soc. of Chem. Ind. 1901.

Daubree has shown that by digestion in a sealed tube with super-heated steam at a high temperature, ordinary glass is decomposed into quartz, wollastonite and alkaline silicate.

True glasses can be made having a wide variation in composition, yet it is a fact that to produce the clearest and most weather-resisting glass, the manufacturers have learned that they cannot depart very much from a given composition. Oxygen ratio, or ratio of bases to acids on the basis of the oxygen content of each, is a factor of prime importance. Starting with a glass in which crystallization is not manifested under ordinary conditions, the points which the ceramist must strive to control are:

1st. The development of these latent crystallizing tendencies.

2nd. To cause the development of crystals in a glassy matrix the physical properties of which, principally expansion and contraction, agree with those of the clay body upon which it is fused, so that both glaze and body will resist all tendency to rupture. A glaze badly crazed, or a dunted body, makes the ware worthless, irrespective of the character of crystals that may have been developed.

As we know practically nothing about the crystallizing value of the several oxides, or combinations of oxides in different proportions, it is very plain why the development of crystals in a glaze is reputed as "freakish," and why but very little importance has been attached to the composition of the amorphous portion of the glaze matrix. Following first one plan of investigation and then another, promising results have been obtained with such varying ratios that experimenters have come to believe that the oxygen ratio or ratio of base to acid is of no consequence in crystalline glaze production, that CaO may or may not be present, and that alkaline earth may be used in any equivalent quantities compatible with the full maturity of the glaze under practical heat treatment. For the reason that

such an unlimited range of choice in materials and ratios is not possible in any other type of glaze or even glass, if for none other, it was believed that before the problem of the production of crystals in a glaze could be studied with any degree of scientific understanding, the true facts concerning possible range in composition should be established. To this end, in the present studies, all other factors such as variation in heat treatment and body composition were eliminated by maintaining them constant throughout.

The table on pages 12-13 gives a synopsis of the plan of investigation of the one factor, viz: Effect of variation in composition.

Crystallizers. Nearly every oxide, and many of the elements are found in nature in a crystalline form. An immense variety of complex silicates are also found in nature as crystals. In ceramic art, the "gold stone," "tiger eye," "aventurine," etc., etc., are crystalline effects produced by supersaturation of a glaze by iron, chromium, etc., in extremely fine particles intimately mixed. Even in the cruder glaze, such as the Bristol and ordinary matt majolica glazes, the opacity in the one and dimness in the other are attributed to crystallization of some element. Having known these facts for some time, ceramists are still unfamiliar with the crystallizing value of the various elements, except in the case of two, zinc oxide and titanium oxide, which give the most pronounced effects. There are cases in which silica and others, lime, for instance, seem to behave as crystallizers. It is certain that opalescent effects which are crystalline in nature, are produced by supersaturation with either lime or silica, and that they occur in nature in a variety of crystalline forms; yet because they have not been known to produce crystals in a glaze, they are not classed as crystallizers. On the basis, then, of the intensity of their crystallizing tendency in a glaze, the list of crystallizers practically consists of but three:—

(1) **Zinc oxide.**
(2) **Titanium oxide.**
(3) **Manganese oxide.**

TABLE II.

Synopsis of General Plan.

Group number	Limits of ZnO	Limits of MnO	Limits of K_2O	Limits of Na_2O
I	1.0—.1	.....	0—.9	.....
II	1.0—.1	.....	0—.9	.....
III	1.0—.1	.....	.....	0—.9
IV	1.0—.1	.....	.....	0—.9
V	1.0—.1	.....	0—.45	0—.45
VI	1.0—.1	.....	0—.45	0—.45
VII	1.0—.1	.....	0—.6	0—.3
VIII	1.0—.1	.....	0—.6	0—.3
IX	1.0—.1	.....	0—.3	0—.6
X	1.0—.1	.....	0—.3	0—.6
XI	.....	1.0—.1	0—.9	.....
XII	.....	1.0—.1	0—.9	.....
XIII	.....	1.0—.1	.....	0—.9
XIV	.....	1.0—.1	.....	0—.9
XV	.....	1.0—.1	0—.45	0—.45
XVI	.....	1.0—.1	0—.45	0—.45
XVII	1.0—.1	.....	0—.45	0—.45
XVIII	1.0—.1	.....	0—.45	0—.45
XIX	1.0—.1	.....	0—.45	0—.45
XX	1.0—.1	.....	0—.45	0—.45
XXI	1.0—.1	.....	0—.45	0—.45
XXII	1.0—.1	.....	0—.45	0—.45
XXIII	1.0—.1	.....	0—.45	0—.45
XXIV	1.0—.1	.....	0—.45	0—.45
XXV	1.0—.1	.....	0—.45	0—.45
XXVI	1.0—.1	.....	0—.45	0—.45
XXVII	1.0—.1	.....	0—.45	0—.45
XXVIII	1.0—.1	.....	0—.45	0—.45
XXIX	1.0—.1	.....	0—.45	0—.45
XXXX	1.0—.1	.....	0—.45	0—.45
XXXI	1.0—.1	.....	0—.45	0—.45
XXXII	1.0—.1	.....	0—.45	0—.45
XXXIII	1.0—.1	.....	0—.9	.....
XXXIV	1.0—.1	.....	.....	0—.9
XXXV	1.0—.1	.....	0—.45	0—.45
XXXVI	.....	1.0—.1	0—.9	.....
XXXVII	.....	1.0—.1	.....	0—.9
XXXVIII	.....	1.0—.1	0—.45	0—.45

TABLE II.

Synopsis of General Plan.

Limits of TiO_2	Limits of SiO_2	Limits Ox. ratios	Limits of numbers	Crystallizing Agents	
.....	.5—1.0	1—2	1— 110	ZnO	
.....	1.0—2.0	2—4	111— 220	ZnO	
.....	.5—1.0	1—2	221— 330	ZnO	
.....	1.0—2.0	2—4	331— 440	ZnO	
.....	.5—1.0	1—2	441— 550	ZnO	
.....	1.0—2.0	2—4	551— 660	ZnO	
.....	.5—1.0	1—2	661— 770	ZnO	
.....	1.0—2.0	2—4	771— 880	ZnO	
.....	.5—1.0	1—2	881— 990	ZnO	
.....	1.0—2.0	2—4	991—1100	ZnO	
.....	.5—1.0	1—2	1101—1210	MnO	
.....	1.0—2.0	2—4	1211—1320	MnO	
.....	.5—1.0	1—2	1321—1430	MnO	
.....	1.0—2.0	2—4	1431—1540	MnO	
.....	.5—1.0	1—2	1541—1650	MnO	
.....	1.0—2.0	2—4	1651—1760	MnO	
.5—0	.0— .5	1	1761—1870	ZnO	TiO_2
.6—0	.0— .6	1.2	1871—1980	ZnO	TiO_2
.7—0	.0— .7	1.4	1981—2090	ZnO	TiO_2
.8—0	.0— .8	1.6	2091—2200	ZnO	TiO_2
.9—0	.0— .9	1.8	2201—2310	ZnO	TiO_2
1.0—0	.0—1.0	2.0	2311—2420	ZnO	TiO_2
1.0—0	.2—1.2	2.4	2421—2530	ZnO	TiO_2
1.0—0	.4—1.4	2.8	2531—2640	ZnO	TiO_2
1.0—0	.6—1.6	3.2	2641—2750	ZnO	TiO_2
1.0—0	.8—1.8	3.6	2751—2860	ZnO	TiO_2
1.0—0	1.0—2.0	4.0	2861—2970	ZnO	TiO_2
1.0—0	1.2—2.2	4.4	2972—3076	ZnO	TiO_2
1.0—0	1.4—2.4	4.8	3082—3186	ZnO	TiO_2
1.0—0	1.6—2.6	5.2	3192—3296	ZnO	TiO_2
1.0—0	1.8—2.8	5.6	3302—3406	ZnO	TiO_2
1.0—0	2.0—3.0	6.0	3412—3512	ZnO	TiO_2
.....	2.0—3.0	4—6	.....	ZnO	
.....	2.0—3.0	4—6	.....	ZnO	
.....	2.0—3.0	4—6	.....	ZnO	
.....	2.0—3.0	4—6	.....	MnO	
.....	2.0—3.0	4—6	.....	MnO	
.....	2.0—3.0	4—6	.....	MnO	

Other glaze ingredients. With the other ingredients, there is not much choice. Alkalies, alkaline earths and acids must be employed. Potash and soda are the only alkalies practically available for this purpose. Calcium, magnesium and barium are the alkaline earths that have been experimented with sufficiently to know their relative value as glaze ingredients. Calcium seems to be the best of the alkaline earth fluxes for glaze purposes. Practical limitations, however, prevent the study of the influence of lime at this time.

Points considered. The whole burden of this investigation is directed toward the settlement of the following questions:

1. The effect of the alkalies, considered singly and together in various proportions, on the development of crystals.

2. The proportional equivalent content of ZnO and conducive to the best development of crystals.

3. The relative crystallizing tendency of zinc, manganese and titanic acid.

4. The character and shape of the crystals induced by manganese.

5. The limits of oxygen ratio permissable in crystalline glazes.

CONSTRUCTION OF THE GROUPS.

The general scheme of construction of the various groups is shown in Table III.

TABLE III.[1]

Showing the relation of glaze formulae to the serial numbers of the glazes.

GROUP I. Oxygen Ratios 1:1—1:2.

Ratios between Zinc Oxide and Potassium Oxide in RO Fluxes. ZnO : K_2O												
1.00 : 0.0	1	11	21	31	41	51	61	71	81	91	101
0.9 : 0.1	2						62				102
0.8 : 0.2	3						63				103
0.7 : 0.3	4	14	24	34	44	54	64	74	84	94	104
0.6 : 0.4	5						65				105
0.5 : 0.5	6						66				106
0.4 : 0.6	7						67				107
0.3 : 0.7	8						68				108
0.2 : 0.8	9						69				109
0.1 : 0.9	10						70				110
	0.50	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	0.95	1.00

Equivalents of Silica.

There are no groups in which titanium is the sole acid, but there are individual glazes in a number of the groups having an oxygen ratio equal to 2 or less, in which TiO_2 is the only acid present.

PREPARATION OF THE GLAZES.

All glazes were fritted at least once before application to the ware. A few of the glazes had to be remelted two, and in a few cases three times, before all of the materials were in complete solution. The case was not uncommon when some of the more infusible material remained in suspension, although the whole was fluid enough to flow freely from the crucible.

Where the alkali content is high and the oxygen ratio low, the fritts are quite soluble in water. In fact, in many cases the fritts were too soluble to allow wet grinding. It seems that some of the soluble salts in the more soluble

[1]The open spaces in the table are supposed to be filled in in arithmetical sequence with those indicated.

fritts are deliquescent to such an extent that in grinding, the powder absorbed moisture from the atmosphere, until they adhered to the pebbles and lining of the mills, making their preparation by either wet or dry grinding impossible.

The soluble glazes are designated in the curves given later, as occurring in the area bounded by solid black lines. These were not made up or tested.

BLENDING CALCULATIONS.

The glazes of each group were obtained by blending between extremes. Since in each group there were two variable factors, i. e., variations in RO composition, and variation in oxygen ratio with each change in RO, there are four extremes.

Referring to the chart given above showing the variation in composition and glaze numbering, the intermediate glazes are obtained by blending glazes 1, 20, 101, and 110. The blending was first made between 1 and 101 and also 20 and 110, i. e., on the basis of oxygen ratio, by the following formula:

$$C = \frac{a(n+1)}{N-1} + \frac{b(n-1)}{N-1}$$

Where a = combining weight of glaze No 1
b = combining weight of glaze No. 101
c = combining weight of required glaze
N = number of variations in oxygen ratio
n = position of required glaze to the right of the left extreme

After having made the blends of the extremes on the basis of oxygen ratio as shown in the top and bottom lines of the chart for group 1, the corresponding glazes in each line are re-blended on the basis of the RO variation by the same formula as given above, except that the notations in the second case are as follows:

a = combining weight of top extreme shown in chart
b = combining weight of bottom extreme
c = combining weight of required glaze
N = number of variations in RO content
n = position of glaze in vertical column

Example of horizontal blending. Given the combining weight of No. 1 as 111, and 101 as 141; required blending mixture for glaze No. 41, where

$$a = 111,\ b = 141,\ N = 11,\ n = 5$$

$$C = \frac{111 \times 6}{10} + \frac{141 \times 4}{10} = 66.6 + 56.4 = 123$$

We would therefore take the proportion of 66.6 grams of No. 1 and 56.4 grams of No. 101 to make No. 41 which has a combining weight of 123.

Example of vertical blending. Given the combining weight of No. 1=111, and No. 7=118.8. To find the blend for No. 3. Here a=111, b=118.8, N=7, n=3.

$$C = \frac{111 \times 4}{6} + \frac{118.8 \times 2}{6} = 74 + 39\ 6 = 113.6$$

Therefore the proportion of extreme 1 and 7 to make 3 is 74 grams of 1. and 39.6 grams of 7. The amount of glaze necessary to cover the trial vase was found to be 16 grams, and if the group is complete, it requires 110x16 or a total of 1760 grams of glaze for each group.

BODY USED.

The body used in these experiments was not chosen because of any special property other than vitreousness at cone 10. It possessed a stony fracture, and was opaque, even when thin. The color generally was pale blue, due to reduction in the biscuit burn. Occasionally, however, it had a pale yellowish tint. No notice was taken of the color of the body, i. e., no discrimination was made in the use of the biscuit, on account of its color.

The composition of the body was as follows:

Florida ball clay	20
Tennessee ball clay[1]	11
Georgia kaolin	21
Flint	13
Spar (Brandywine)	35

[1]This clay had theapproximate formula, $0.2K_2O\ 1.0Al_2O_3\ 3.9SiO_2$.

The body was blunged in the form of a slip in ball mills having a capacity of about 4 gallons. The mills were run for about 30 minutes at 45 revolutions per minute, this amount of grinding being sufficient to slake the clay, and thoroughly blend all the body ingredients.

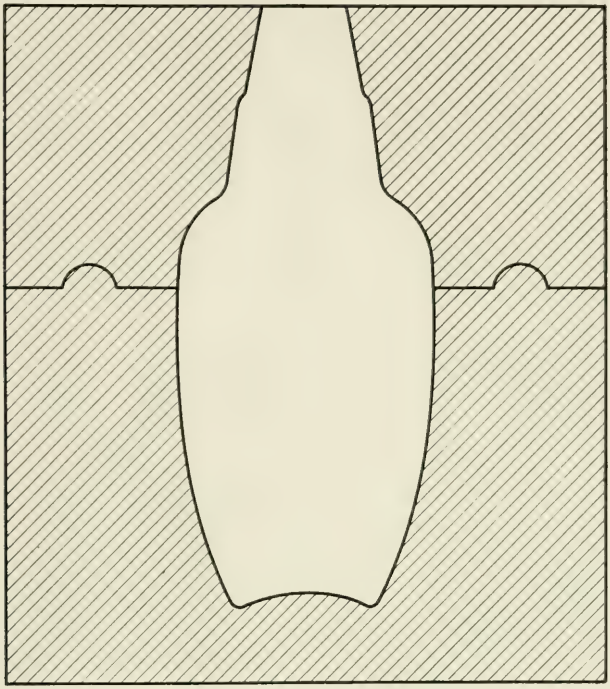
After grinding, the body was sieved through a 40-mesh screen and stored in large stoneware jars. No attention was paid to the length of time that the slip remained in the jars, hence some portions of the mixture as used were aged longer than others, obtaining as a consequence slight variation in character of biscuit.

SHAPE OF TRIAL PIECE.

For the development of crystals, a heavy coating of glaze must be applied to the biscuit. As a consequence of this application, and of the excessive fluidity of the glazes when at the state of fusion required to permit the best development of crystals, provision must be made for the large amount that naturally flows off the vertical sides of the vases. Further, as was shown by the saggar bottom exhibited by Mr. Gates at the Birmingham meeting of the American Ceramic Society, crystals seem to develop best on flat surfaces where the glaze accumulates in thick layers and flowage is impossible. It was thought imperative, therefore, that both a vertical and a flat surface should be provided. These conditions were attained in the combination of vase, ring stilt, and saucer.

This combination of vase, ring and saucer was 4½″ over all in height and 3″ in diameter. The vases were cast in a two-part mould, the ring pressed in a mould similar to handle moulds, and the saucer batted out in a one-piece mould. The shape of the vase produced is shown in the following plate:

TRANS. AM. CER. SOC. VOL. IX PURDY AND KREHBIEL, PLATE I



Mold employed in making the Vases used as Trial Pieces in the Crystalline Glaze Experiments.

BISCUIT FIRING.

Aside from the first few burns, which of necessity were all biscuit, no separate biscuit burns were made. After a stock of biscuit had been accumulated, one sagger of biscuit in each glost burn was found sufficient to furnish all that was required. Six saggers were placed in the kiln, one for the cone and pyrometer, one and sometimes two saggers for biscuit, the remaining three or four being reserved for the glaze. In the biscuit the vases were placed touching one another. The biscuit rings were generally placed in the cone sagger on top of a bung exposed to the full play of the flames, and the saucers were placed wherever opportunity offered.

GLOST FIRING.

Saggers. The saggers used in these experiments were made with extra thick walls to prevent sudden fluctuation in temperature at times when the fire doors were opened, as well as to insure the slow steady cooling so necessary to the best production of crystals. Each sagger is large enough to hold eleven or twelve vases. The sides of the glaze saggers were washed with a mixture of alkaline flux, zinc and flint. The bottom of the sagger was coated with a mixture of equal parts of bone ash and flint.[1]

Placing of ware in kiln. The saggers were placed in the kiln in two bungs, the side of the front bung being next to the wicket. The bungs were three saggers high, nearly filling the space in the firing chamber. The cone or trial sagger was placed in the middle of the front bung. Inasmuch as the top sagger of the front bung seemed to be in the place least favorable for slow cooling, it was used exclusively for biscuit. The bottom sagger in the front and all the saggers in the rear bung were used for glaze.

Number of trials in burn. With one sagger for the cone, and one for biscuit, it was possible to burn only 44 to 48 glost trials in a single burn.

Heat Treatment. The cones placed in the trial sagger were Nos. 5, 7, 8, 9 and 10. In each sagger of glost, there was placed a shortened cone 10. There was developed a difference of two cones between the inside and outside of the sagger, due probably to the difference in rate of cooling. It was found that when the heat was raised, as shown in the firing curves, until cone 8 in the trial sagger was fused, cone 10 would be down in all of the glost saggers. This regularity in heat distribution was obtained in practically every burn.

Firing. Time was not taken in the beginning to thoroughly study the conditions favorable to the best develop-

[1]This mixture has been used by Professor Binns to advantage in preventing the slagging of the sagger bottoms by flowing glaze.

ment of crystals. The method of firing in the first few burns differed therefore from the method used in the later burns, as shown in the following summary:

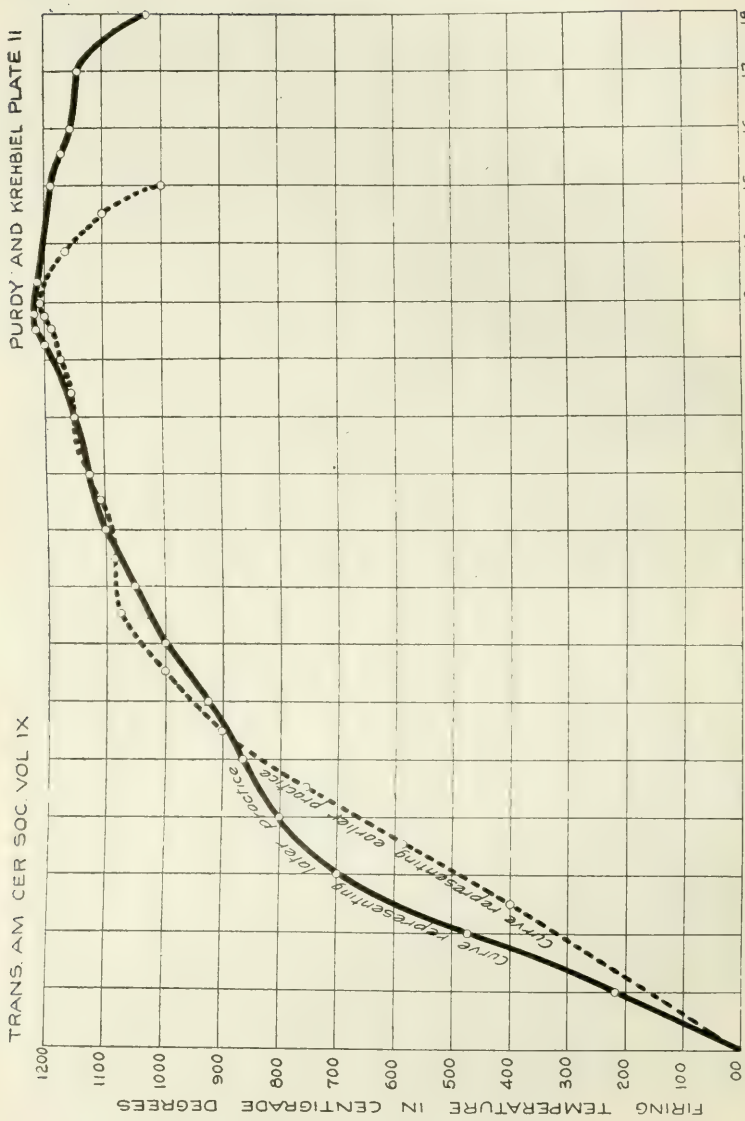
First few Burns.

Length of time expended in firing and cooling, 18 to 22 hours.
Fuel used—soft coal.
Thickness of bed—thin.
Cooled by slow firing.
Results—irregularity.

Later Burns.

Length of time expended in burning and cooling to 200°C, 15 to 16 hours.
Fuel used—coke.
Thickness of bed—3 to 4 inches.
Cooled by sealing kiln, and pulling fire.
Results—Perfect control.

Time—Temperature Treatment. The accompanying curves, Plate II, show the time-temperature treatment, which was obtained in practically every burn. Considerable importance is justly attached to the time-temperature treatment of crystalline glazes. In a preliminary burn, good crystals were developed in glazes that had been successfully used on a commercial scale, and the time-temperature treatment plotted. It was found, however, that this curve could not be followed strictly in the later burns, and hence there were considerable irregularities in this regard from burn to burn. Further work with the more promising glazes is planned to determine the time-temperature treatment best suited to the development of crystals in the University of Illinois trial kiln. (For drawing, see page 25, U. of I. Bulletin No. 12.



Time-Temperature Curves, showing Rate of Firing and Cooling in the Crystalline Glaze Experiments.

One fact in connection with the time-temperature treatment was developed in these studies, which permitted the shortening of the total time required for each burn, viz., that the rate of raising heat did not seem to affect the character of crystallization, unless the heat raised so rapidly as not to permit complete fusion of the entire glaze mass. Inasmuch as each glaze used in the various blends had been rendered homogeneous by fritting, and the thick saggers and heavy brick work of the kiln necessarily made the raising of heat a comparatively slow process, it may be said that under these conditions the heat may be raised as rapidly as possible.

The cooling. The question of cooling seems the all-important one. Slow cooling was accomplished by two methods, first, by continuing the firing with a bare spot on the grate, and, second, by drawing the fire and sealing the kiln completely. The second method proved to be the better, for the results by the first method were far from consistent from burn to burn.

Difficulties encountered. First, each glaze was worked up into a paste with gum of tragacanth by spatula on a glass slab, without having previously mixed the blended portions. This method of treatment gives good results when sufficient pains are taken, but it sometimes happened that a careless operator would not thoroughly blend the several portions of the glaze, and consequently the more fusible portions would be unevenly distributed, giving rise to a warty appearance of the glaze when burned.

Second: The base of the vase was so small that if not setting squarely on the ring, or if the ring was not well made, the vase would often tumble over.

Third: Because each vase was placed on a ring and then the whole placed on a saucer, it was found necessary to set each piece separately. The kiln walls being 18 inches in thickness, the four burns per week kept the kiln so hot that it made the placing of these 48 trial pieces a very difficult task. It often happened, therefore, that the vases

were not set squarely in the saucers, and consequently were easily jarred over when the sagger was covered either by another sagger, or by a hiller.

ZINC OXIDE AS A CRYSTALLIZING AGENT.

From researches in the past, it has been demonstrated that zinc oxide is, in small quantities, not only as active a flux as lime, but also that as a flux, it is more favorable to the development of crystallization. Seger's cone 4[1], for example, is rendered considerably more fusible by the addition of only a "trace" of zinc oxide. Bristol glazes, which are similar in composition to cone 4, have zinc oxide substituted in part for lime. In amounts less than 0.3 equivalents it acts as a flux, producing clear glazes, but any addition over this amount produces incipient crystallization as indicated by the resulting opacity. Whether or not it is a zinc compound that crystallizes, is not known. It is sufficient for the purpose at hand to note that incipient crystallization is a consequence of the presence of zinc oxide in excess of the amount that produces maximum fusibility in the glaze mixtures. It is therefore obvious that instead of the alkaline earth CaO, as in ordinary glass, it would be more conducive to the development of crystals to use ZnO.

Noting that the successful fritted glazes as given in Table I contain no CaO, and not knowing its influence on the development of crystals, it was deemed advisable not to complicate our preliminary survey of this field by incorporating it in our glaze compositions. After having determined the alkali-zinc-silica mixture that has the greatest crystallizing tendency, then, it was thought, would be early enough to begin to study the influence of lime. In Groups I to VI inclusive, therefore, the study is confined to alkali-zinc-silica combinations.

[1]Trans. Amer. Cer. Soc. Vol. VIII, p 163.

GROUP I

Subdivisions into Series on Basis of SiO_2 Molecular Content		Variation in RO Content within each Series			Oxygen Ratio of Each Series		Glaze Number in Each Series
Series No.	SiO_2 Content	No.	ZnO	K_2O	Series No	O. R.	a-j
1	0.50	a	1.0	0.0	1	1.0	1- 10
2	0 55	b	0.9	0.1	2	1.1	11- 20
3	0.60	c	0.8	0.2	3	1.2	21- 30
4	0.65	d	0.7	0.3	4	1.3	31- 40
5	0.70	e	0.6	0.4	5	1.4	41- 50
6	0.75	f	0.5	0 5	6	1.5	51- 60
7	0.80	g	0.4	0.6	7	1.6	61- 70
8	0.85	h	0.3	0.7	8	1.7	71- 80
9	0.90	i	0.2	0.8	9	1.8	81- 90
10	0.95	j	0.1	0.9	10	1.9	91-100
11	1.00				11	2.0	101-110

Fusibility. When the RO contains less than 0.4 K_2O, irrespective of acid content, the glazes are infusible at cone 10.

Solubility. With more than 0.6 K_2O, in the case of oxygen ratio 1 : 1 and 0.7 K_2O, in the case of oxygen ratio 1 : 2, the glazes are soluble.

Luster. All the matured glazes in this group have bright glossy luster. No matts are developed. Glaze No. 7 having a molecular formula of 0.4 K_2O, 0.6 ZnO, 0.5 SiO_2 approached the nearest to a matt finish.

Crazing and shivering. All the matured glazes were crazed in such extremely fine meshes, irrespective of acid content, as to render this defect almost unnoticeable to the naked eye.

Crystallization. In glazes having an RO of

$$\begin{cases} 0.4 - 0.5\ ZnO \\ 0.6 - 0.5\ K_2O \end{cases}$$

irrespective of acid content, minute crystals develop, especially on horizontal surfaces where the glazes accumulate in thick masses. These minute needle-like crystals are so interlaced and so thickly bunched together, that in many cases they lose their individuality.

None of the glazes of this group were fired in a check burn, but judging from our experience with the titanium crystalline glazes, it is thought that under certain firing conditions (not now known) there would be developed on the vertical surface of the vase the same thick and irregular mixture of minute needle-like crystals that in our own burns appeared only in the saucers, producing either a matt or aventurine effect. It is, however, evident from the glossiness of the glazes on the vases, and the consistent absence of crystals on the upright faces throughout the whole series, that the conditions of firing would be too exacting to warrant the use of any of the glazes of this group for matt, crystalline or aventurine effects.

GROUP II.

Sub-division into Series on Basis of SiO_2 Molecular Content		Variation in RO Content within each Series			Oxygen Ratio of Each Series		Glaze Numbers in Each Series
Series No.	SiO_2 Content	No.	ZnO	K_2O	Series No.	O R.	a-j
1	1.0	a	1.0	0.0	1	2.0	111–120
2	1.1	b	0.9	0.1	2	2.2	121–130
3	1.2	c	0.8	0.2	3	2.4	131–140
4	1.3	d	0.7	0.3	4	2.6	141–150
5	1.4	e	0.6	0.4	5	2.8	151–160
6	1.5	f	0 5	0.5	6	3.0	161–170
7	1.6	g	0.4	0.6	7	3.2	171–180
8	1.7	h	0.3	0.7	8	3.4	181–190
9	1.8	i	0.2	0.8	9	3.6	191–200
10	1.9	j	0.1	0 9	10	3.8	201–210
11	2.0				11	4.0	211–220

Fusibility. When the RO contains less than 0.2 K_2O, irrespective of the acid content, the glazes are infusible. With acid content of 1.0—1.2 SiO_2 (oxygen ratio 2.0 to 2.4) and RO composition of 0.2 K_2O, 0.8 ZnO, the glazes while glossy are not sufficiently fusible to flow smoothly.

Solubility. The only glazes of this group that are so soluble as to render them impractical on a commercial scale are those in which the RO contains 0.9 K_2O.

Luster. All the matured glazes had bright glossy luster, except No. 116, which has the molecular formula

$$\left.\begin{matrix}0.5\ K_2O\\0.5\ ZnO\end{matrix}\right\}\ 1.0\ SiO_2 \quad (OR = 2)$$

Crazing and shivering. All the matured glazes in this group crazed. With oxygen ratio of 1.2 the crazing was in fine meshes, while with oxygen ratio of 4 the crazing was relatively coarse.

Crystallization. As shown in Plate No. III, the glazes in which crystals are developed have an RO range of

$$\left\{\begin{matrix}0.3 - 0.5\ K_2O\\0.7 - 0.5\ ZnO\end{matrix}\right.$$

irrespective of acid content.

The character and mode of occurrence of crystals are the same in this group as in Group I, except in the case of glazes No. 155 and 184, having respectively the molecular formula

$$\left.\begin{matrix}0.6\ ZnO\\0.4\ K_2O\end{matrix}\right\}1.4\ SiO_2 \quad \text{and} \quad \left.\begin{matrix}0.7\ ZnO\\0.3\ K_2O\end{matrix}\right\}1.7\ SiO_2$$

in which there is a slight tendency to segregate into radial clusters. Most of the crystals on these two vases are individual bars scattered without definite direction throughout the glaze matrix.

Conclusions from Groups I *and* II. From the fact that the glazes of these two groups were burned in five separate burns, in allotments of about 40 glazes to each burn, and gave consistent results throughout each of the two groups, it would seem that the following statements were substantiated beyond a doubt:

First. While crystals were developed at all oxygen ratios between 1 and 4, the most extensive development and the largest crystals occurred with oxygen ratios ranging from 2.2 to 3.0 and with RO content of

$$\left\{\begin{matrix}0.3\ \text{to}\ 0.5\ K_2O\\0.7\ \text{to}\ 0.5\ ZnO\end{matrix}\right.$$

Within this oxygen ratio range, the glazes on the vertical faces of the vases are crystalline to some extent, while at

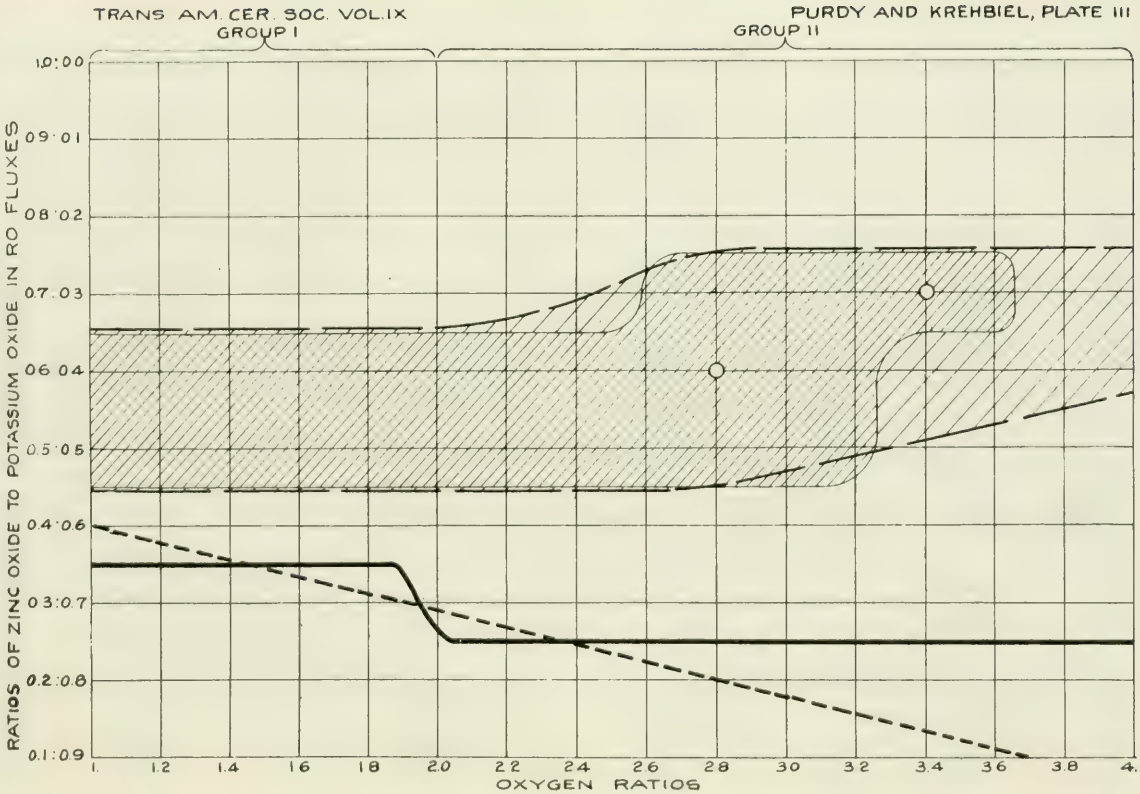


Chart showing results of crystalline glaze experiments, using zinc and potash as RO fluxes. Area below heavy black line contains glazes found to be soluble in water. Area below heavy dotted line shows probable extent of soluble glaze limits. Heavy shading shows area in which crystalline glazes were produced. Light shading shows area in which crystalline glazes may be expected. Circles indicate position of glazes furnishing good crystals.

other oxygen ratios the crystals occur only on the horizontal faces, where the glazes have accumulated in thick masses.

Second. Notwithstanding that commercial crystalline glazes free from TiO_2, quoted in Table I, fall in Group II, it is a fact that in no case are crystalline effects developed to a commercially note-worthy extent.

Third. The high coefficient of expansion and contraction of the potash-zinc glazes is strikingly shown in the fact, that even with an oxygen ratio of 4, the craze lines are fine and interlace, forming meshes about the size of those in 20 mesh screens. This may explain in part the reason that the commercial glazes before cited are so high in silica.

Fourth. It is evident that K_2O-ZnO-SiO_2 compounds cannot fulfill the requirements of ceramists.

GROUP III.

Sub-divisions into Series on Basis of SiO_2 Molecular Content		Variation in RO Content within Each Series			Oxygen Ratio of Each Series		Glaze Number in Each Series
Series No.	SiO_2 Content	No.	ZnO	Na_2O	Series No.	O. R.	a–j
1	0.50	a	1.0	0 0	1	1.0	221–230
2	0 55	b	0.9	0.1	2	1.1	231–240
3	0.60	c	0 8	0.2	3	1.2	241–250
4	0.65	d	0.7	0.3	4	1.3	251–260
5	0.70	e	0.6	0.4	5	1 4	261–270
6	0.75	f	0.5	0.5	6	1.5	271–280
7	0.80	g	0 4	0.6	7	1.6	281–290
8	0.85	h	0 3	0.7	8	1.7	291–300
9	0 90	i	0.2	0.8	9	1.8	301–310
10	0.95	j	0.1	0.9	10	1.9	311–320
11	1.00				11	2 0	321–330

Fusibility. The glazes of this group, having Na_2O as the alkaline flux, are more fusible than the K_2O glazes of Group I. As a consequence, in this group there can be used 0.1 Eqv. more of ZnO than in Group I, and yet produce glazes sufficiently fluid to cover the whole surface of the vases.

When the RO contains less than 0.3 Na_2O, irrespective of the acid content, the glazes are infusible at cone 10.

Solubility. With more than 0.6 Na_2O, in the case of oxygen ratio 1 : 1, and 0.7 Na_2O, in the case of oxygen ratio 1 : 2, the glazes are soluble.

Luster. As compared with those of Group I the glazes of this group exhibit a dimness which in many cases would be styled "matt." In no instances in this group was there a bright glossy glaze developed.

Glazes having RO content of

$$\left\{\begin{matrix} 0.3 - 0.4\ Na_2O \\ 0.2 - 0\ 6\ ZnO \end{matrix}\right.$$

are decidedly "matts," irrespective of acid content.

Crazing and shivering. Fine mesh crazing, as noted in Group I, was developed also in this group. No shivering developed.

Crystallization. As shown in Plate No. IV, the glazes having as an RO

$$\left\{\begin{matrix} 0.3 - 0.5\ Na_2O \\ 0.7 - 0.5\ ZnO \end{matrix}\right.$$

irrespective of acid content, develop crystalline structure to a notable extent. The glazes containing less than 0.5 ZnO melted to clear glasses, but still having less gloss than the K_2O glasses.

The crystals developed in the glazes of this group, while needle-like, are comparatively large and symmetrically arranged in radiating groups from definite centers—like the spokes around a hub. In the case of the potash glazes, the needle-like crystals are massed like a pile of loose pins, no systematic arrangement being observable in any instance.

Owing to the consistent manner in which matt surfaces and crystalline effects were developed in this group, notwithstanding the fact that they were burned in three installments, as were those of Group I, the statement that Na_2O will, in glazes of this type, permit of a more extensive development of crystals than K_2O seems warranted. It is also evident that on a commercial basis, none of the glazes of this group could be used for the production of

either matts or crystalline glazes, owing to the fact that neither are developed to a commercially noteworthy extent.

GROUP IV.

Sub-division into Series on Basis of SiO_2 Molecular Content		Variation in RO Content within Each Series			Oxygen Ratio in Each Series		Glaze Numbers in Each Series
Series No.	SiO_2 Content	No.	ZnO	Na_2O	Series No.	O. R.	a–j
1	1.0	a	1 0	0.0	1	2.0	331–340
2	1 1	b	0.9	0.1	2	2.2	341–350
3	1.2	c	0.8	0.2	3	2.4	351–360
4	1.3	d	0.7	0.3	4	2.6	361–370
5	1.4	e	0.6	0.4	5	2.8	371–380
6	1 5	f	0 5	0.5	6	3.0	381–390
7	1.6	g	0.4	0.6	7	3.2	391–400
8	1.7	h	0.3	0.7	8	3.4	401–410
9	1.8	i	0 2	0 8	9	3.6	411–420
10	1·9	j	0.1	0.9	10	3.8	421–430
11	2.0				11	4.0	431–440

Fusibility. The infusible area is the same in this, as in Group III.

Solubility. The soluble area is confined to those glazes having Na_2O content of 0.9 Eqv.

Luster. The glazes of this group have a more brilliant gloss than those of the preceding group. Glazes having an RO of 0.3 K_2O, 0.7 ZnO, irrespective of oxygen ratio, are either so minutely crystalline as to be matts, or have large crystals in a glassy matrix. This production in the zinc-soda groups of small crystals causing a matt effect, or large crystals causing a characteristic crystalline effect, would seem to be a function of the burning, rather than of glaze composition.

In all of the matured glazes of this group, those lowest in oxygen ratio are the dimmest.

Crazing and shivering. The same phenomena of fine mesh crazing with the lower oxygen ratios, and relatively coarse mesh crazing with the higher, as in Group II, are noted in this group.

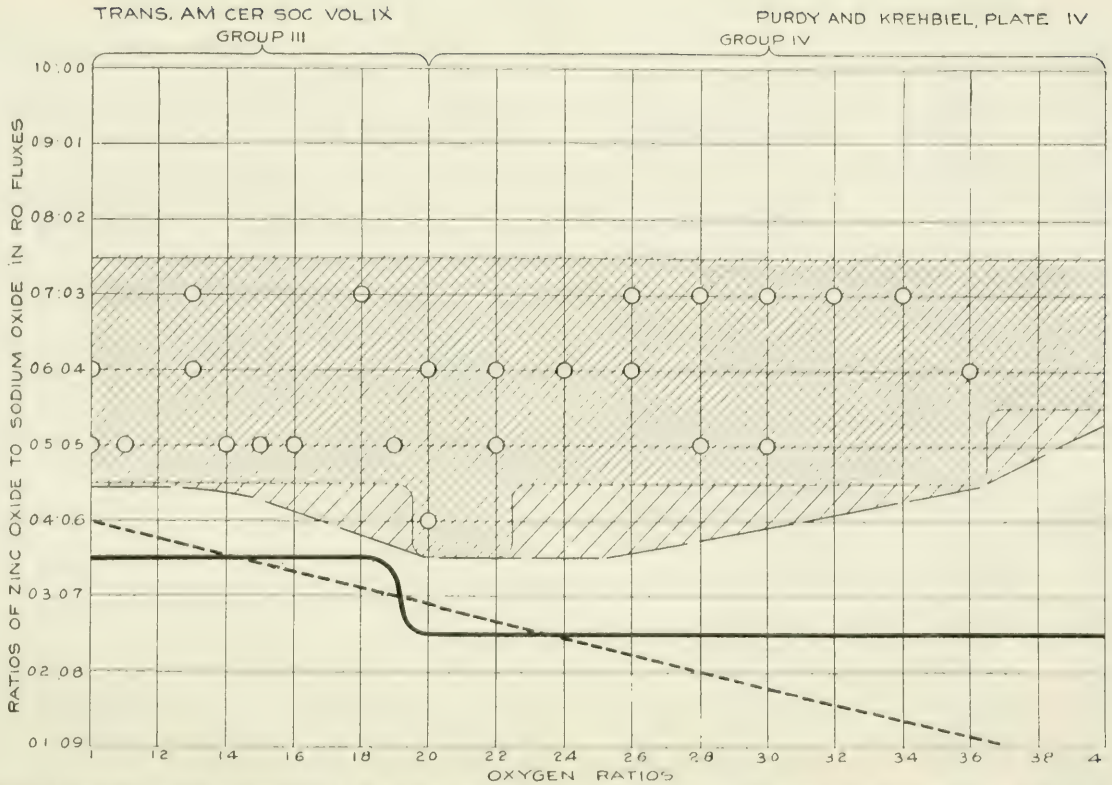


Chart showing results of crystalline glaze experiments, using zinc and soda as RO fluxes. Area below solid black line contains glazes found to be soluble in water. Area below heavy dotted line shows probable extent of soluble glaze area. Heavy shading shows area in which crystalline glazes were produced. Light shading shows area in which crystalline glazes may be expected. Circles indicate position of glazes furnishing good crystals.

Crystallization. The range in composition of glazes showing either a developed or latent crystallization is narrower in this group than in Group III, and about the same as in Group II. The crystallizing tendency, however, within this range is more pronounced in Group IV than in Group II, and, where developed, the crystals are quite large, the needles being in some instances, particularly in glaze No. 355, 0.4 Na_2O, 0.6 ZnO, 1.2 SiO_2, over an inch in length.

The most pronounced crystallization occurs within oxygen ratios 2.2 to 3.2. At oxygen ratios less than 2.2, the crystals are so minute as to produce matt effects, and at ratios higher than 3.2 the glazes, while glossy, show but very little tendency to crystallize, except on the shoulder of the vases.

Conclusions from Groups III *and* IV. In these two groups, as in the case of Groups I and III, crystals were developed with all oxygen ratios ranging from 1 to 4, but the most pronounced and best devloped crystals occurred with oxygen ratios 2.2 to 3.2. Within these ratios also, the crystallization seems to be more persistent, and less a function of the burning conditions.

In glazes 374, 384 and 394, having the molecular formula 0.4 Na_2O, 0.6 ZnO, 1.4 to 1.6 SiO_2, large clusters of beautiful crystals were produced that would be considered as commercially attractive.

Development of crystals in the soda groups, III and IV, was more pronounced than in the potash groups, I and II. This checks observed facts in the phenomenon of devitrification of glasses. "It[1] has been determined that glasses rich in soda devitrify faster than those rich in potash."

[1]Van Hise, Treatise on Metamorphism, Mon. No. XLVII, U. S, Geol Surv., p. 248.

GROUP V.

Sub-division into Series on Basis of SiO_2 Molecular Content		Variation in RO Content within Each Series				Oxygen Ratio in Each Series		Glaze Numbers in Each Series
Series No.	SiO_2 Content	No.	ZnO	K_2O	Na_2O	Series No.	O. R.	a-j
1	0.50	a	1.00	0.00	0.00	1	1.0	441–450
2	0.55	b	0.90	0.05	0.05	2	1.1	451–460
3	0.60	c	0.80	0.10	0.10	3	1.2	461–470
4	0.65	d	0.70	0.15	0.15	4	1.3	471–480
5	0.70	e	0.60	0.20	0.20	5	1.4	481–490
6	0.75	f	0.50	0.25	0.25	6	1.5	491–500
7	0.80	g	0.40	0.30	0.30	7	1.6	501–510
8	0.85	h	0.30	0.35	0.35	8	1.7	511–520
9	0.90	i	0.20	0.40	0.40	9	1.8	521–530
10	0.95	j	0.10	0.45	0.45	10	1.9	531–540
11	1.00					11	2.0	541–550

Fusibility. When the RO contains less than 0.4 KNaO, the glazes are infusible at cone 10, irrespective of acid content.

Solubility. With more than 0.6 KNaO in the case of oxygen ratio 1, and 0.7 KNaO in case of oxygen ratio of 2, the glazes are soluble. This confirms the results noted in Group I.

Luster. All the matured glazes are matts, except those having the molecular formula

$$\left.\begin{matrix}0.4\ ZnO\\0.3\ K_2O\\0.3\ Na_2O\end{matrix}\right\}\ 1.3\ \text{to}\ 2.0\ SiO_2$$

These glazes are clear bright glasses without the least sign of crystallization.

Crazing and shivering. Crazing in fine meshes, but no shivering are noted in this group.

Crystallization. The essential difference between the crystals in the zinc-potash and zinc-soda glazes in the almost total absence of symmetrical grouping in the former, and almost perfect symmetry in the latter. In this group, where the potash and soda are present in equal equivalents, these two crystallizing habits seem to operate simultaneously, but independently of one another, causing a matt

surface. Under an ordinary magnifying glass there may be no crystalline structure noted, but when examined under a higher power glass, the crystals are observed to be irregularly arranged, i. e., here a symmetrical grouping and there a heterogeneous mixture. The force tending to develop the characteristic crystals of the zinc-soda mixture seems, however, to be the stronger, for wherever the crystals are developed sufficiently to be distinguished by the naked eye, they are arranged in symmetrical groups similar to those described in the soda glazes.

GROUP VI.

Sub-division into Series on Basis of SiO_2 Molecular Content		Variation in RO Content within Each Series				Oxygen Ratio in Each Series		Glaze Numbers in Each Series
Series No.	SiO_2 Content	No.	ZnO	K_2O	Na_2O	Series No.	O. R.	a-j
1	1.0	a	1.00	0.00	0.00	1	2.0	551-560
2	1.1	b	0.90	0.05	0.05	2	2.2	561-570
3	1.2	c	0.80	0.10	0.10	3	2.4	571-580
4	1.3	d	0.70	0 15	0.15	4	2.6	581-590
5	1.4	e	0.60	0.20	0 20	5	2.8	591-600
6	1.5	f	0 50	0.25	0 25	6	3.0	601-610
7	1.6	g	0 40	0.30	0.30	7	3.2	611-620
8	1.7	h	0 30	0.35	0.35	8	3.4	621-630
9	1.8	i	0.20	0.40	0.40	9	3.6	631-640
10	1.9	j	0 10	0.45	0.45	10	3.8	641-650
11	2.0					11	4.0	651-660

Fusibility, Solubility. The fusible and soluble areas of this group correspond exactly with those of Group II.

Luster. Most of the matured glazes of this group exhibit a surface that is neither as glossy as the potash, nor as dim as the soda glazes. Mattness is most pronounced with oxygen ratios ranging from 2.0 to 2.6.

Crazing and shivering. All the matured glazes of this group are crazed, the craze mesh being coarser with each increase in acid content.

Crystallization. Considering the most promising results shown in Groups III and IV, it is indeed very puzz-

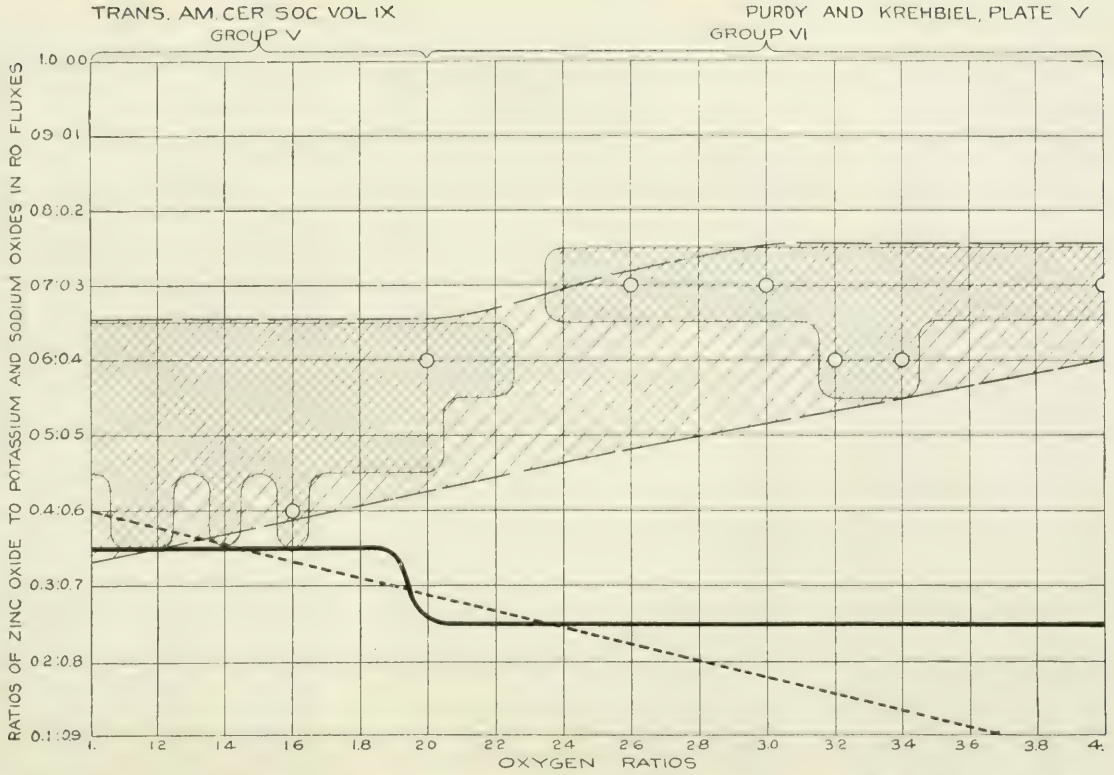


Chart showing results of crystalline glaze experiments, using zinc and potash and soda as RO fluxes. Area below black line contains glazes found to be soluble in water. Area below heavy dotted line shows probable extent of soluble glaze limits. Heavy shading shows areas in which crystalline glazes were produced. Light shading shows area in which crystalline glazes may be expected. Circles indicate position of glazes furnishing good crystals.

ling to note that the glazes of this group show so little tendency to crystallize. No large clusters of crystals were developed.

Conclusions from Groups V and VI. The crystalline areas in Groups V and VI are shown in Plate No. V, on page 36.

It is impossible to state why there was so little crystallization in these double alkali mixtures. The same treatment throughout was given to these groups as to the former, so that the limited extent of crystallization cannot be charged wholly to the conditions of firing or cooling. The only analogous phenomena that the writers have personally seen is the attempt by Mr. Jones to obtain in our laboratories a crystalline mass by supersaturation of a mixture of several salts in solution, as reported by him in his paper on efflorescence. Supersaturation of a single salt produced definite crystals, but with a mixture of salts the crystalline nature, if it possessed any, could not be determined. It would seem far-fetched to attempt the explanation of the dearth of crystal development in these groups on any such basis, but the facts in these two experiments, the one in ordinary aqueous solution and the other in an igneous silicate solution, coincide so closely that we cannot do otherwise than give the involved idea some consideration.

OXIDE OF MANGANESE AS A CRYSTALLIZING AGENT.

The following manganese groups are similar in construction to those of the preceding zinc groups. They were planned and nearly all made up before the results obtained in the zinc groups had been studied. In this we were fortunate, for by blindly planning these groups, much that is of interest, as will be seen, would have otherwise not been brought out.

GROUP XI.

Sub-division into Series on Basis of SiO_2 Molecular Content		Variation in RO Content within Each Series			Oxygen Ratio of Each Series		Glaze Number in Each Series
Series No.	SiO_2 Content	No.	MnO.	K_2O	Series No.	O. R	a-j
1	0.50	a	1.0	0.0	1	1.0	1101–1110
2	0.55	b	0.9	0.1	2	1.1	1111–1120
3	0.60	c	0.8	0.2	3	1.2	1121–1130
4	0.65	d	0.7	0.3	4	1.3	1131–1140
5	0.70	e	0.6	0.4	5	1.4	1141–1150
6	0.75	f	0.5	0.5	6	1.5	1151–1160
7	0.80	g	0.4	0.6	7	1.6	1161–1170
8	0.85	h	0.3	0.7	8	1.7	1171–1180
9	0.90	i	0.2	0.8	9	1.8	1181–1190
10	0.95	j	0.1	0.9	10	1.9	1191–1200
11	1.00				11	2.0	1201–1210

Fusibility. The fluxing power of manganese manifested itself in member a of each series where the glazes, while not smooth, have flowed sufficiently to cover the bottom of the saucer. On comparing the members a of this group with those of Groups I and III, it would seem as though MnO is a more powerful flux than ZnO. The remaining members of this group fuse to a smooth coating at cone 10.

Solubility. With a potash content of 0.4 or more, and oxygen ratio of 0.5, and also with 0.7 or more K_2O and an oxygen ratio of 1.0, the glazes are soluble in water.

Crazing and shivering. There is practically no crazing or shivering noted in this group.

Luster. There are no bright glazes in this group. All are dark brown, but streaked with purple in those of higher, and light "flesh" brown in those of lower alkaline content.

Crystallization. In Plate VI is shown the crystalline area of this group.

The character of crystals, i. e., their habits of growth, vary considerably in a seemingly erratic manner. For instance, in glaze 1144, 1163, 1164, 1172, and 1173, the crystals are projected from the surface in globular form, while

in the other instances, the crystals are concentrically developed and lie wholly within the plane of the glaze matrix. In the case of the globular crystals, the greatest development is near the base of the vase, while the non-globular forms are developed mostly at the top of the vase.

Under a magnifying glass, the crystals in both instances are similar in general character.

GROUP XII.

Sub-division into Series on Basis of SiO_2 Molecular Content		Variation in RO Content within Each Series			Oxygen Ratio of Each Ratio		Glaze Numbers in Each Series
Series No.	SiO_2 Content	No.	MnO	K_2O	Series No.	O. R.	a-j
1	1.0	a	1.0	0.0	1	2.0	1211–1220
2	1.1	b	0.9	0.1	2	2.2	1221–1230
3	1.2	c	0.8	0.2	3	2 4	1231–1240
4	1.3	d	0.7	0.3	4	2.6	1241–1250
5	1.4	e	0.6	0 4	5	2.8	1251–1260
6	1.5	f	0.5	0.5	6	3 0	1261–1270
7	1.6	g	0.4	0.6	7	3.2	1271–1280
8	1.7	h	0.3	0.7	8	3.4	1281–1290
9	1.8	i	0.2	0.8	9	3.6	1291–1300
10	1.9	j	0.1	0.9	10	3 8	1301–1310
11	2.0				11	4.0	1311–1320

Fusibility. All glazes having an oxygen ratio 1 : 2 are fusible at cone 10. When the oxygen ratio has been increased to 1 : 4.0 the glazes containing less than 0.3 equivalents of K_2O are infusible.

Solubility. All glazes of this group containing more than 0.7 equivalents of K_2O are soluble.

Luster. While no "matts" occur in this group, none of the glazes containing more MnO or less K_2O than 0.5 equivalents, can be said to be bright glazes.

Notwithstanding the fact that with low K_2O we have a high MnO content, there are no evidences in this or the preceding group of any separating out of the manganese forming the metallic lustrous effect that would appear in a raw lead glaze, if more than 0.2 equivalents of MnO were used. If anything, the maximum density of color in these groups is produced with RO, 0.5 MnO, 0.5 K_2O.

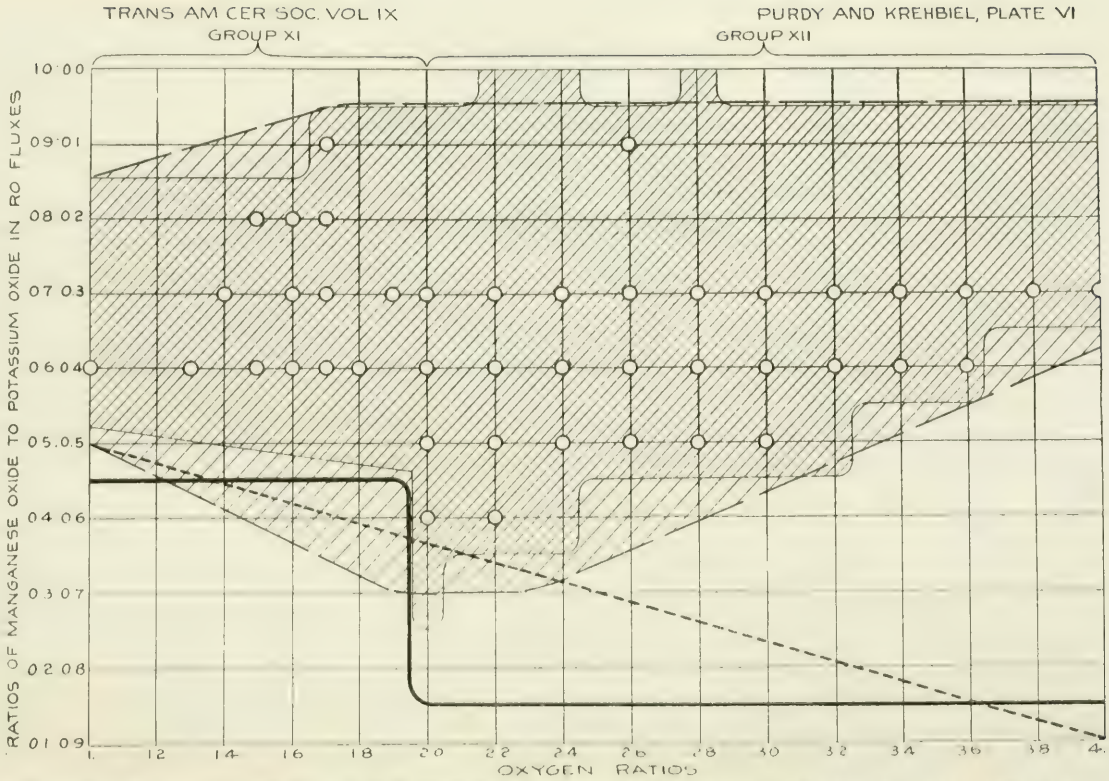


Chart showing results of crystalline glaze experiments, using manganese and potash as RO fluxes. Area below black line contains glazes found to be soluble in water. Area below heavy dotted line shows probable extent of soluble glaze limits. Heavy shading shows area in which crystalline glazes were produced. Light shading shows area in which crystalline glazes may be expected. Circle indicate position of glazes furnishing good crystals.

Crystallization. In Plate No. VI is shown the crystalline area of this group.

The crystals in glazes having an oxygen ratio of 2.0—2.6 are very consistent in their manner of growth, and, in repeated burns, in their extent of development. Data is not at hand from which to judge of the influence of varying heat treatment and fire gases on the development of crystals in this acid range. So pronounced is the crystallizing tendency in this acid range, that in nearly every instance, the crystals have projected from the surface of the vase in globular forms.

With higher acid content, the crystals are all within the plane of the glaze matrix, and assume beautiful purple concentric forms.

Color. Rich purple tints are developed in the following glazes:

$$\left.\begin{matrix} 0.4\ MnO \\ 0.6\ K_2O \end{matrix}\right\} 1.7 \text{ to } 2.00\ SiO_2$$

$$\left.\begin{matrix} 0.3\ MnO \\ 0.7\ K_2O \end{matrix}\right\} 1.4 \text{ to } 2.00\ SiO_2$$

Groups XIII *and* XIV.

Groups XIII and XIV were similar in construction to the two preceding groups, differing from them only in the use of Na_2O in place of K_2O.

The general features of Groups XIII and XIV are similar to those of the corresponding K_2O groups. Their crystalline areas are represented in Plate No. VII.

The habit of the crystals developing into the nodular forms is not so pronounced in the Na_2O glazes as in those of the K_2O group, but occurs in the same relative glaze composition in these as in the K_2O groups. Crystals, when lying wholly within the same plane as that of the glaze matrix, are more fan-like, and the spaces between the radial extension are webbed or filled in more than is the case with the K_2O glazes.

Purple tints occur in glazes of the same relative composition in these groups as in the potash groups, but are much lighter in tint.

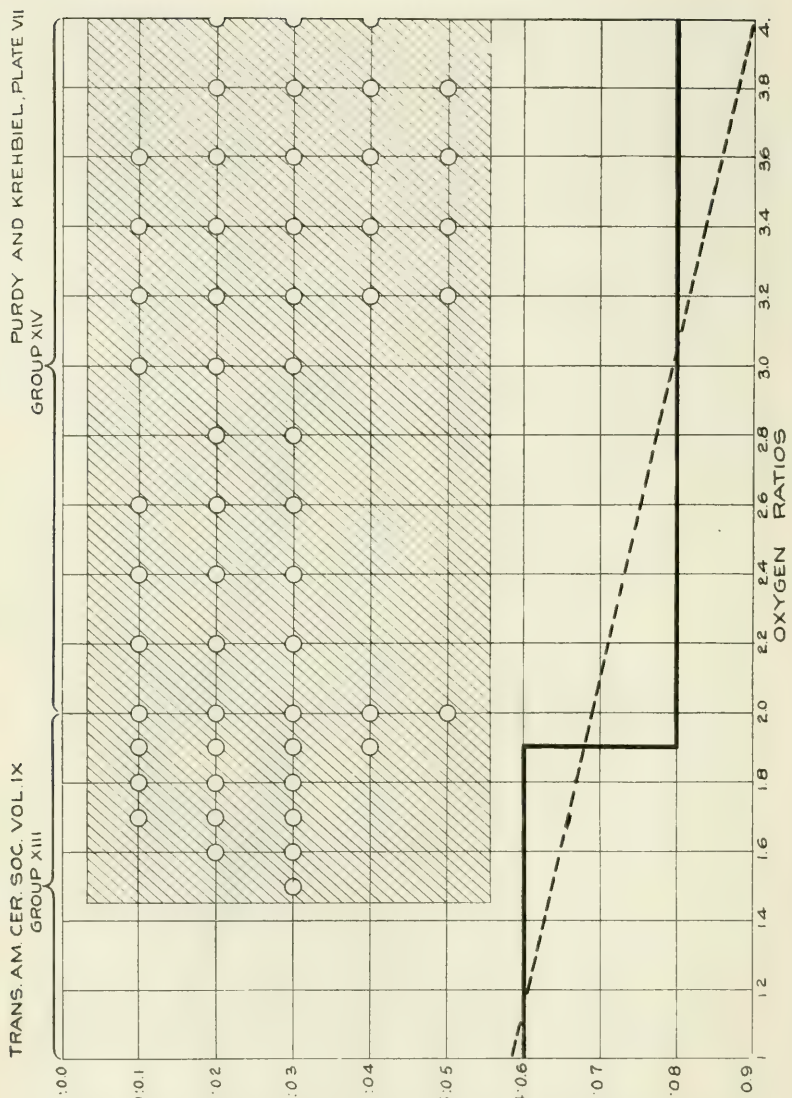


Chart showing results of crystalline glaze experiments, using manganese and soda as RO fluxes. Area below heavy black line contains glazes found to be soluble in water. Area below dotted line shows probable extent of soluble glaze limits. Heavy shading shows area in which crystalline glazes were produced. Circles indicate position of glazes furnishing good crystals.

Under favorable firing conditions, glazes with 0.5 Eqv. MnO and high acid content, assume a permanent soft black velvet-like texture that is very striking. The writers are unable to explain this phenomenon, owing to the fact that its development has been proven not to be wholly a function of either the composition or firing conditions. In intensity of color and softness of texture, it surpasses the most perfect black tile, made by the use of recovered manganese oxide, that the writers have ever seen. Vases exhibiting this beautiful black effect are in the majority of cases entirely free from definite crystals of notable size, and yet there is occasionally a vase having this smooth black texture as a background out from which stand purple crystals ⅛ of an inch in diameter.

Summary of Groups XI, XII, XIII, XIV.

1. In both the potash and soda groups, the most intense crystallizing development occurs between oxygen ratios 1.8 and 2.6, or acid content of 0.9 to 1.3.

2. The crystals developed in the K_2O, MnO, SiO_2 matrix are purple in color, and when not globular assume circular forms. In these circular clusters, light colored spiral lines, which are more or less regular in their spiral growth, produce a damask effect that is truly beautiful. In Plate XXI, page 67, is shown the globular growth of crystals in glaze No. 1173, having the formula

$$\left.\begin{matrix}0.8\ MnO\\0.2\ K_2O\end{matrix}\right\}0.85\ SiO_2$$

and in Plate XX, page 66, the spiral growth in glaze No. 1155, having the formula

$$\left.\begin{matrix}0.6\ MnO\\0.4\ K_2O\end{matrix}\right\}0.75\ SiO_2$$

In Plate XXII, page 68, are shown crystals that are just beginning to pass from the flat to the globular form. This is developed in glaze No. 1235, having the formula

$$\left.\begin{matrix}0.6\ MnO\\0.4\ K_2O\end{matrix}\right\}1.2\ SiO_2$$

3. In contrast to the purple crystals of the K_2O mixtures, the soda crystals stand out as white, or at least light-

tinted forms on the brown and black backgrounds. In these, the concentric or spiral rings are entirely absent. The crystals, even when globular, have the circular crystals arranged in radial clusters that, with the shading from light to dark tints and the silky luster, look very much like pansy blossoms.

4. The soda crystals, unlike any of those in K_2O glazes, are in some instances indistinct, and show merely as a lighter tinted spot below the surface of the glaze, producing a mottled effect that is superb. As these hidden crystals develop, light-tinted concentric rings form around the incipient crystals, increasing in both size and intensity, until when the crystal appears at the surface, the concentric rings are no longer apparent and the radial pansy-like clusters of the acicular crystals appear. This transition from the hidden incipient crystals, to a large well-developed cluster of crystals, is displayed on a single vase in a large number of instances, and particularly in those glazes that have an oxygen ratio of 2.6 to 3.0.

5. With 0.2 eqv. of manganese, the purple tint produced is much lighter and less rich in the soda mixtures than in the potash.

6. For variety of crystallizing phenomena, and variety of tints developed, the soda mixtures surpass those containing potash.

7. As shown by contrasting Plates VI and VII, the crystallizing areas in the potash-manganese glazes are as large as are those of the soda manganese, but the soda-manganese crystals are more persistent in their growth.

GROUP XV.

Sub-division into Series on Basis of SiO_2 Molecular Content		Variation in RO Content within Each Series				Oxygen Ratio of Each Series		Glaze Numbers in Each Series
Series No.	SiO_2 Content	No.	MnO	K_2O	Na_2O	Series No.	O. R.	a-j
1	0.50	a	1.00	0.00	0.00	1	1.0	1541–1550
2	0.55	b	0.90	0.05	0.05	2	1.1	1551–1560
3	0.60	c	0.80	0.10	0.10	3	1.2	1561–1570
4	0.65	d	0.70	0.15	0.15	4	1.3	1571–1580
5	0.70	e	0.60	0.20	0.20	5	1.4	1581–1590
6	0.75	f	0.50	0.25	0.25	6	1.5	1591–1600
7	0.80	g	0.40	0.30	0.30	7	1.6	1601–1610
8	0.85	h	0.30	0.35	0.35	8	1.7	1611–1620
9	0.90	i	0.20	0.40	0.40	9	1.8	1621–1630
10	0.95	j	0.10	0.45	0.45	10	1.9	1631–1640
11	1.00					11	2.0	1641–1650

In solubility, fusibility, luster and freedom from crazing and shivering, the group corresponds with Group XI.

Crystallization. Globular crystals, while developed with the higher oxygen ratios and manganese content as in Group XI, are not so pronounced and are more confined to definite areas. In Group XI these globular crystals occur irregularly at any oxygen ratio, while in this group, they occur only at the oxygen ratios of 1.9 and 2. On the whole, the growth of nodular crystals is less pronounced in this than in Group XI. In this respect Group XV resembles Group XIII. The crystalline area and the glazes in which there is a development of good crystals are indicated in Plate No. VIII.

In general character, the crystals resemble more those of the soda-manganese crystals, but have a little more indefinite character. In many instances, and this is not confined to any given area, the crystals are nearly devoid of color, i. e. they are very light. In many others, there seems to be a mixture of white and purple crystals interfering with one another in development in a way that results in a most striking variegated fawn-colored effect. This, how-

ever, occurs only on a portion of a vase, and often a vase, as for example in glaze No. 1646,

$$\left.\begin{matrix}0.5\ MnO\\0.5\ KNaO\end{matrix}\right\}1.0\ SiO_2$$

a large area of this variegated or mottled fawn effect will be fringed by small radial fan-like crystals resembling in detail those occurring in the soda-manganese glazes. In glaze No. 1636,

$$\left.\begin{matrix}0.5\ MnO\\0.5\ KNaO\end{matrix}\right\}0.95\ SiO_2$$

the crystallizing tendency results in blurred, but more or less round, white spots scattered over a brown background.

The greater number and the more pronounced crystals occur in glazes having as an RO

$$\left.\begin{matrix}0.5\ MnO\\0.5\ KNaO\end{matrix}\right\}$$

GROUP XVI.

Sub-division into Series on Basis of SiO_2 Molecular Content		Variation in RO Content within Each Series				Oxygen Ratio of Each Series		Glaze Numbers in Each Series
Series No.	SiO_2 Content	No.	MnO	K_2O	Na_2O	Series No	O. R.	a-j
1	1.0	a	0.00	0.00	0.00	1	2.0	1651-1660
2	1.1	b	0.90	0.05	0.05	2	2.2	1661-1670
3	1.2	c	0.80	0.10	0.10	3	2.4	1671-1680
4	1.3	d	0.70	0.15	0.15	4	2.6	1681-1690
5	1.4	e	0.60	0.20	0.20	5	2.8	1691-1700
6	1.5	f	0.50	0.25	0.25	6	3.0	1701-1710
7	1.6	g	0.40	0.30	0.30	7	3.2	1711-1720
8	1.7	h	0.30	0.35	0.35	8	3.4	1721-1730
9	1.8	i	0.20	0.40	0.40	9	3.6	1731-1740
10	1.9	j	0.10	0.45	0.45	10	3.8	1741-1750
11	2.0					11	4.0	1751-1760

The fusibility and solubility area of this group have the same relative extent and position as in groups XI and XIV. The color is dark brown or black, except in the case of low manganese and high silica.

Crystallization. The occurrence and extent of crystallization developed in this group is shown in Plate No.

VIII. The crystals are not as well developed as in groups XI and XIV, where only one alkali is used. In fact, the combat between the crystallizing forces tending to develop the two types characteristic of the K_2O glazes on the one hand and the Na_2O glazes on the other, has resulted in that dense black velvety finish before noted. On some of the vases, the characteristic crystals of the K_2O glazes are developed, and on others those of the Na_2O, but on none do the two types occur together.

Conclusions on the Manganese Groups XI, XVI.

First. While rich effects are produced with K_2O as the only alkali, and with a combination of the two alkalies, the most extensive development and the most beautiful effects are obtained with a simple MnO, Na_2O, SiO_2 mixture.

Second. Manganese-alkali-silica combinations have in these experiments proven to better support the development of crystals than the zinc-alkali-silica combinations.

Third. For variety of effects and richness in play of dark and light colors, the soda mixtures prove to be the best.

Fourth. For rich purples, the potash mixtures have proven to give the best results.

Fifth. The development of what has been termed "globular" crystals will be of special interest in further study of this problem, in that they can be easily detached and analyzed. The writers have in a speculative way, assumed various compositions for these globular crystals, on the assumption that they are similar in composition to some of nature's manganese crystals like rhodonite ($MnSiO_3$), in an attempt to ascertain whether these manganese glazes in many cases have not been carried to too high a temperature to produce the best results. On every hypothetical assumption, the non-crystalline portion of these glazes proved to be similar in make-up to many glazes reported as maturing at cone 1 or less. Close adherence to the original plan of burning all glazes at cone 10, however, prevented the following of these suggestions at the lower

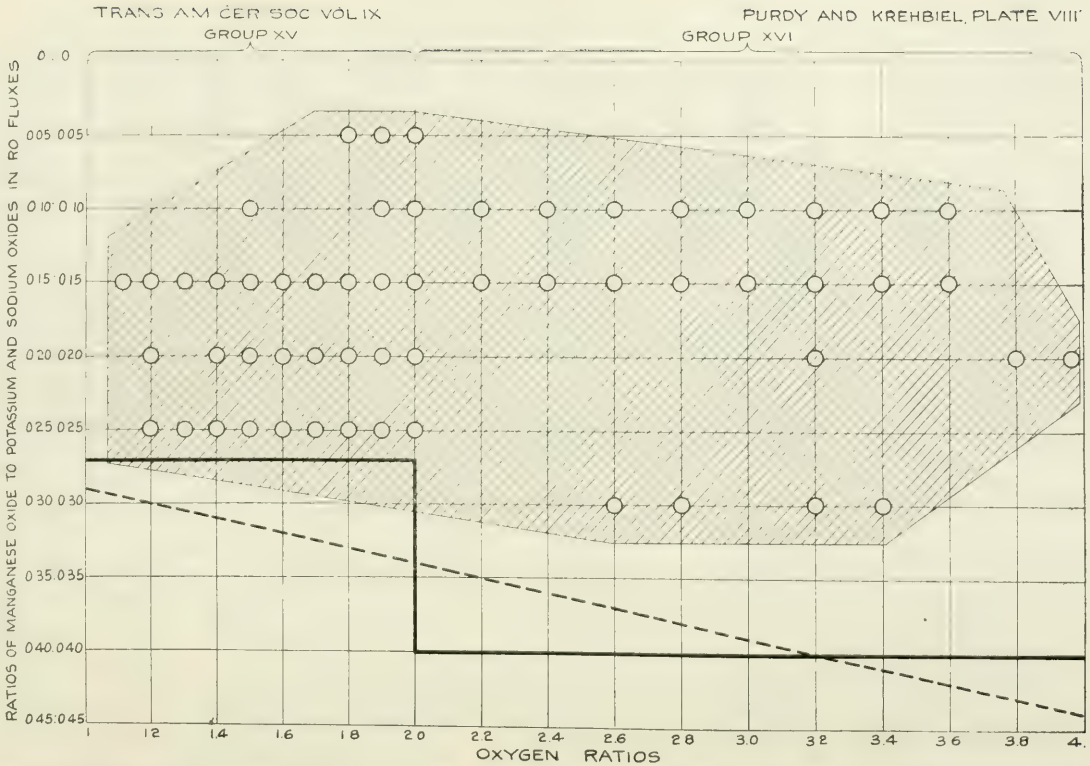


Chart showing results of crystalline glaze experiments, using manganese and potash and soda as RO fluxes. Area below heavy black line contains glazes found to be soluble in water. Area below heavy dotted line shows probable extent of soluble glaze limits. Heavy shading shows area in which crystalline glazes were produced. Circles indicate position of glazes furnishing good crystals.

heats. After determining the composition of the globular crystals, there will no doubt be disclosed a very fruitful field for further research along these lines.

Sixth. The use of manganese as a crystallizing agent, so far as the writers can learn, has never been exploited in this country before. References have been made in various places to the possibility of its use, from the fact that the Japanese have claimed it was used in the production of their magnificent purple crystals. Being to the writers an untried crystallizing agent, no further studies were projected at this time, but for future studies it is planned to try various zinc-manganese-alkali-titanium and silica combinations, which, it is believed, will be productive of many new and highly interesting phenomena in crystalline glazes.

TITANIC OXIDE AS A CRYSTALLIZING AGENT.

In most of the reported researches on crystalline glazes, considerable stress has been laid upon the strong influence of titanium in the development of crystals. In view of the erratic manner in which titanium behaves as a flux in clays and pottery bodies, and in view of the widely divergent reports as to the manner in which crystals grow under its influence, it was thought well to study the effect of additions of titanium in several equivalent amounts at different oxygen ratios, using as a basis the zinc-alkali-silica mixtures of Groups I—VI.

If titanium had the power ascribed to it, either of augmenting the crystallization of other substances, or by entering into combination with the crystallizing ingredients, of producing greater constancy in habit of the crystals, the writers thought that its true functions in these connections would surely be revealed in the scheme presented below.

These groups were planned, and a few of them burned, before the writers had opportunity to study the results obtained from Groups I to VI inclusive. A more detailed scheme was therefore executed than would have perhaps seemed justifiable. Foreseeing this possibility, all groups

of the lower oxygen ratios were not made up. Considering the surprising results obtained, however, it is considered fortunate that the titanium groups were carried out in the detail shown in table IV, page 51.

Group XVII.

All glazes of this group containing more than 0.4 equivalents of KNaO are soluble, irrespective of the nature of acid content.

All glazes of this group containing less than 0.3 K_2O are infusible.

Acicular crystals in the ground mass are visible to the naked eye, even in those mixtures which are too infusible to flow, and cover the entire surface of the vase. In fact, it would seem in many instances, as though the whole mass crystallized in its entirety, thus preventing its becoming sufficiently fluid to attain a smooth surface. No commercially attractive crystals were developed in this group.

Group XIX.

In this group, all glazes containing more than 0.4 equivalents of KNaO are soluble.

In this, as well as in Group XVII, TiO_2 does not appear to operate as a flux. In fact, those glazes in which silica is the only acid present, are more fusible than any in which TiO_2 has been added at the expense of some of the SiO_2.

In Plate No. IX is shown the soluble, fusible and crystalline areas of this group.

The crystals in this group are a trifle more developed, and fewer in number. In fact, on the vertical faces of the vases, the crystals may be said to be fascicularly grouped, each group assuming its individual plane and direction of development. On the shoulders of many of the vases included in the crystalline area shown in Plate No. IX, the crystals are arranged in radial clusters. Notwithstanding the fact that the crystals of this group have definite habits, they are so small that they may be called micro-crystals.

TABLE IV.

Showing the constitution of the groups and series of glazes projected for the investigation of the influence of titanic acid as a crystallizing agent.

Division into Groups, on Basis of Oxygen Ratio, With a variation in acid content in each series.																Division into Series	Division into Members on basis of RO Content.			
Group XVII O.R.—1.0		Group XIX O.R.—1.4		Group XXI O.R.—1.8		Group XXIII O.R.—2.4		Group XXIV O.R.—2.8		Group XXV O.R. 3.2		Group XXVI O.R.—3.6		Group XXVII O.R.—4.0						
TiO_2	SiO_2	TiO_2	SiO_2	TiO_2	SiO_2	TiO_2	SiO_2	TiO_2	SiO_2	TiO_2	SiO_2	TiO_2	SiO_2	TiO_2	SiO_2		ZnO	K_2O	Na_2O	Member No.
0.50	0.00	0.70	0.00	0.	0 00	1.0	0 2	1.0	0 4	1.0	0 6	1.0	0 8	1.0	1.0	1	1.00	0.00	0.00	a
0.45	0.05	0.63	0.07	0.81	0 09	0.9	0 3	0.9	0 5	0.9	0.7	0.9	0 9	0 9	1.1	2	0.90	0.05	0 05	b
0 40	0.10	0.56	0.14	0.72	0.18	0.8	0 4	0.8	0 6	0 8	0 8	0.8	1.0	0.8	1 2	3	0.80	0.10	0.10	c
0 35	0.15	0.49	0.21	0.63	0 27	0.7	0 5	0.7	0.7	0.7	0.9	0.7	1.1	0.7	1 3	4	0.70	0.15	0.15	d
0 30	0.20	0.42	0.28	0.54	0.36	0 6	0.6	0 6	0 8	0.6	1.0	0.6	1 2	0.6	1 4	5	0.60	0.20	0.20	e
0.25	0.25	0.35	0.35	0.45	0 45	0.5	0.7	0.5	0.9	0.5	1.1	0.5	1 3	0.5	1 5	6	0.50	0.25	0.25	f
0.20	0.30	0.28	0.42	0.36	0.54	0 4	0.8	0 4	1.0	0.4	1 2	0 4	1.4	0 4	1 6	7	0.40	0.30	0.30	g
0.15	0.35	0.21	0.49	0.27	0.63	0 3	0.9	0 3	1 1	0 3	1 3	0 3	1 5	0 3	1 7	8	0.30	0.35	0.35	h
0 10	0 40	0.14	0.56	0.18	0.72	0 2	1.0	0 2	1 2	0.2	1 4	0 2	1 6	0 2	1 8	9	0.20	0.40	0.40	i
0.05	0.45	0.07	0.63	0.09	0 81	0 1	1.1	0 1	1 3	0 1	1 5	0 1	1 7	0.1	1.9	10	0.10	0.45	0.45	j
0.00	0.50	0.00	0.70	0 00	0 90	0 0	1.2	0 0	1 4	0 0	1 6	0 0	1 8	0 0	2.0	11				

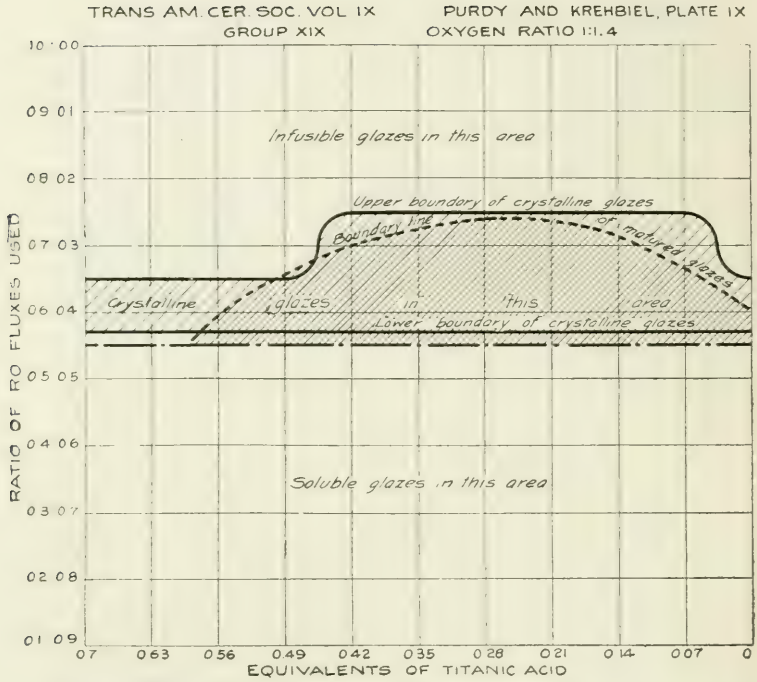


Chart showing results of crystalline glaze experiments, using zinc and the alkalies as RO fluxes, and titanic acid as part or all of the acid portion. Oxygen Ratio of all glazes on this chart 1:1.4.

The glazes that gave the most promising results are those having the molecular composition of

$$\left.\begin{matrix} 0.6\ ZnO \\ 0.4\ KNaO \end{matrix}\right\} \begin{matrix} 0.21 \text{ to } 0.49\ SiO_2 \\ 0.49 \text{ to } 0.21\ TiO_2 \end{matrix}$$

Group XXI.

In this group, maximum fusibility is attained when the ratio of SiO_2 to TiO_2 is 4 : 1. Glaze No. 2283, having the formula

$$\left.\begin{matrix} 0.8\ ZnO \\ 0.2\ KNaO \end{matrix}\right\} \begin{matrix} 0.72\ SiO_2 \\ 0.13\ TiO_2 \end{matrix}$$

has fully matured; in fact, fused sufficiently to have run off the vase to a considerable extent.

On vertical faces the crystals are fascicular, but do not intertwine or overlap one another. On horizontal faces, however, the crystals are more needlelike and so thickly interlaced that the mass has a dull rough appearance.

Crystals of fair size are developed as shown on Plate X. In plates XXIX, XXX and XXXI, pages 75, 76 and 77, are shown the character of these crystals.

While it is evident that a small addition of TiO_2 renders the zinc-alkali-silica mixtures having low oxygen ratios more fusible, the TiO_2, or possibly the titanate that is formed, does not remain in solution, but is merely suspended in the glassy matrix. In fact, many of the glazes of Group XXI resemble, in effect, raw tin glazes.

There is no evidence in the three titanic oxide groups so far studied, that the titanic oxide enters into combination with the crystallizing compounds. On the contrary, the crystals developed in glaze 2306, shown in plate XXXI, and which contains no TiO_2, are typical of the crystals developed in all of the groups which contain TiO_2. Further, crystals seem to develop only in the transparent glossy patches, and not in those portions which are opaque. A mottled effect, i. e. brown splotches, on a white or clear background, is so characteristic of the titaniferous glazes, that it seems plausible that the titanic acid mole-

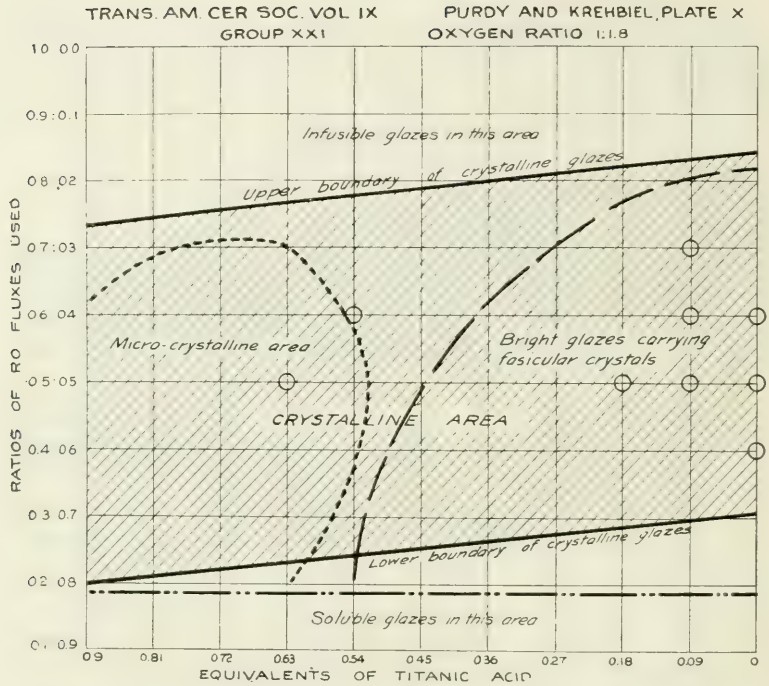


Chart showing results of crystalline glaze experiments, using zinc and the alkalies as RO fluxes, and titanic acid partly or wholly substituting silica in the acid portion. Oxygen ratio of all glazes in this chart 1:1.8. Circles indicate position of glazes furnishing good crystals.

cules have clustered together in small groups. These small groups are seldom, if ever, crystalline, and appear to have nothing in common with the clear matrix that surrounds them.

That TiO_2 conduces to crystallization is shown by the fact that the glazes which contain the largest molecular equivalent of TiO_2 are a mass of minute crystals. As silica decreases, and titanic acid increases in equivalent amounts, the matrix assumes the characteristic dark brown tint of the titanium compounds. These dark brown masses are devoid of gloss, and yet when KNaO amounts to 0.7 equivalents, the mass becomes sufficiently fluid at cone 10 to overflow the saucer on which the vase is placed. Whether this fluidity is due to fusion of the whole mass into a molten matrix, of to the fusion of simply a zinc-alkaline silicate, by which the titanium compounds are carried in mechanical suspension, is not known. It is plain, however, that the minute crystals which are formed in these dark brown masses, and are devoid of color, resemble those developed in the glazes which are free from titanium.

Plate No. X shows the general results obtained in Group XXI.

Group XXIII.

In general characteristics, this group resembles XXI. The crystals are larger and, for the first time, have passed from the fascicular to clustered growths.

In plates XXXII, XXXIII, XXXIV and XXXV, pages 78, 79, 80 and 81, are shown characteristic specimens of the crystals developed in this group.

As the titanic acid content increases from 0 to 0.2 equivalents, crystals increase in size and number. But as the titanic acid is increased beyond 0.2 equivalents, although the crystals continue to increase in number, they decrease rapidly in size until, as shown in Plate XI, when the titanic acid content amounts to 0.6 equivalents the crystals are microlitic in character, and the mass so thoroughly crystallized as to be devoid of gloss. When the

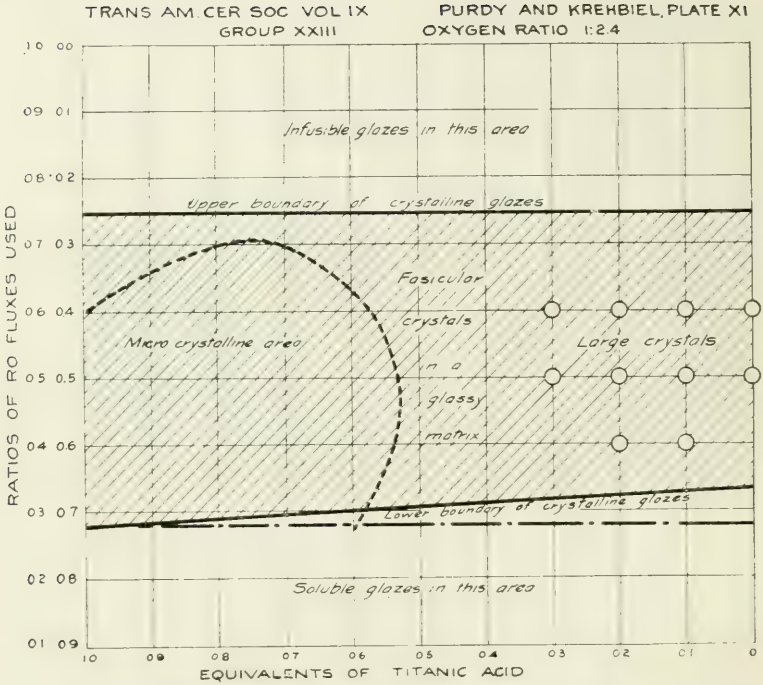


Chart showing results of crystalline glaze experiments, using zinc and the alkalies as RO fluxes, and titanic acid partly substituting silica in the acid portion. Oxygen ratio of all glazes on this chart 1:2.4. Circles indicate position of glazes furnishing good crystals.

titanic acid has increased to 0.9 equivalents, the whole mass has crystallized to a dull porphyritic mass.

Group XXIV.

The essential features of this group are shown in Plate XII.

In this group, the true role of TiO_2 is better shown than in any of the preceding. The sharp line of demarkation between the area in which crystals are developed in clusters, and the area in which the crystals, while more numerous, pass from fascicular habits of growth to independent thread-like units, is considered as being due entirely to the influence of increasing content of TiO_2, and not to accidental factors such as firing conditions, etc.

Plate XXXVII, page 83, shows crystals that developed in glaze No. 2613 which has the molecular composition of

$$\left.\begin{matrix} 0.8\ ZnO \\ 0.2\ KNaO \end{matrix}\right\} 0.2\ TiO_2 \\ 1.2\ SiO_2$$

In no two glazes were the crystal clusters identical. This diversified manner of development in zinc-titanium glazes has been mentioned by other experimentors, but we are still unable to explain the phenomenon.

In the introductory remarks, reference was made to the fact that crystals have been developed in the cold under the influences of vapor, from window glass that was to all appearances a homogeneous mass. The writers are unaware of any experiments designed to show the possible diversity in character of crystals developed under the influence of different vapors, but it seems plausible that such a diversity would be probable. At all events, the fact that ceramists have laid considerable stress upon maintaining oxidizing conditions when burning crystalline glazes, shows that considerable importance has been attached to the composition of the vapors in which the crystals are developed. Further, some writers insist that the character of the vapor fumes should be controlled by heavily glazing

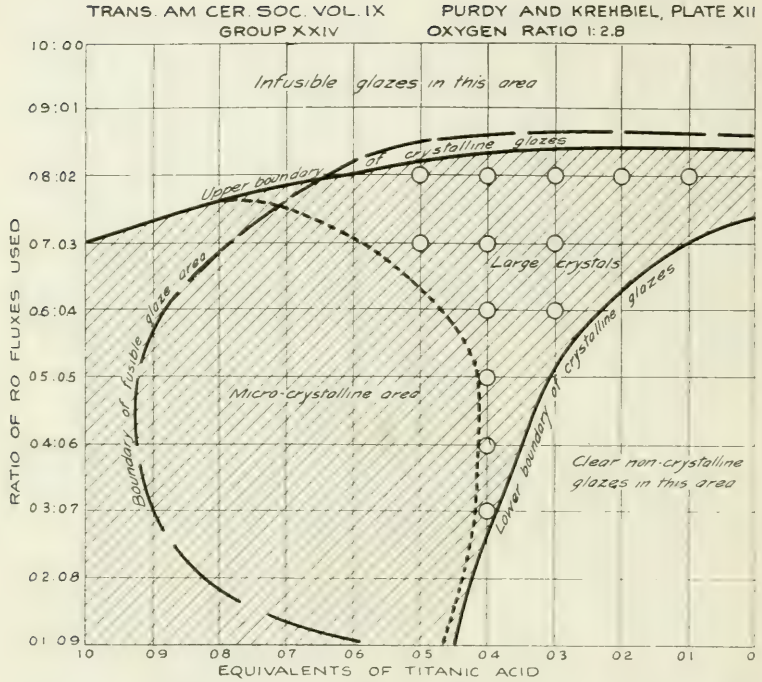


Chart showing results of crystalline glaze experiments, using zinc and the alkalies as RO fluxes, and titanic acid partly substituting silica in acid portion. Oxygen ratio of all glazes in this chart 1:2.8. Circles indicate position of glazes furnishing good crystals.

the sides of the sagger with the same kind of glaze as that on the ware. The writers, however, have not been able to observe that the crystals developed in a tightly luted and heavily glazed sagger were any more consistent in their habits of growth than those developed in a poorly glazed, unluted sagger.

It is noted that in this group, the most consistent development of large crystals occurs when the RO contains 0.8 equivalents of ZnO. In all groups so far studied, the large clusters were most consistently developed when the ZnO content was 0.5 equivalents. Further, in the case of the preceding titanic acid groups, the crystals attained their best development when the ratio of TiO_2 to SiO_2 was 1 : 4, but in this group, the oxygen ratio of which is 2.8, they attain their best development when the ratio of TiO_2 to SiO_2 is 0.5 to 0.9 or 1 to 1.9. That there is some significance in the fact that as the titanic acid increases, the zinc must be increased in order to permit of extensive growth of crystals, cannot be questioned. Can it be possible that zinc oxide, which, as was demonstrated in Groups I to VI, has a pronounced crystallizing tendency, must be increased in order to overcome the tendency of titanic acid to develop micro-crystals? This is indeed an important consideration, but one which the writers feel unable to discuss from data at hand.

Group XXV.

The oxygen ratio of this group (3.2) is higher than that with which, in the zinc and manganese groups, there was attained maximum development of crystals. In this respect, the results obtained in this group check those obtained in the analogous zinc and manganese glazes. Considering the fact that the several glazes having this oxygen ratio were not burned at one time, and that, no matter what the crystallizing agent employed happened to be, all agreed in having a very limited tendency to develop either large individual or extensive groups of crystals, it must be con-

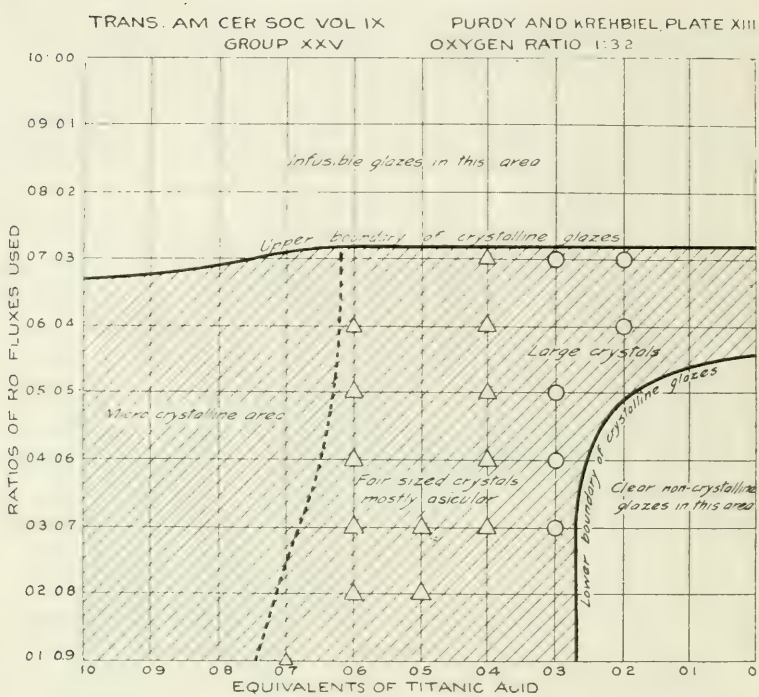


Chart showing results of crystalline glaze experiments, using zinc and the alkalies as RO fluxes, and titanic acid partly substituting silica in the acid portion. Oxygen ratio of all glazes in this chart 1:3.2. Circles indicate position of glazes furnishing good crystals. Triangles indicate glazes which made acicular crystals on vertical surfaces and large crystals on horizontal surfaces.

ceded that the results are not accidental but rather are characteristic of glazes of this type and oxygen ratio.

In Plate XIII are shown the salient features developed in this group.

Group XXVI.

The results obtained in this group are so similar to those obtained in the preceding group that they do not require elaboration.

In Plate XIV are shown the general results.

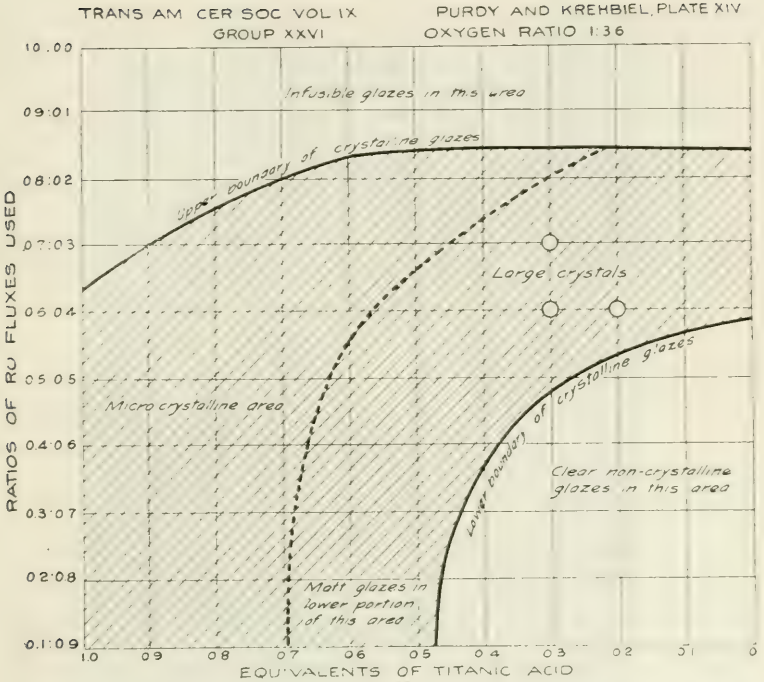


Chart showing results of crystalline glaze experiments, using zinc and the alkalies as RO fluxes, and titanic acid partly substituting silica in the acid portion. Oxygen ratio of all glazes on this chart 1:3.6. Circles indicate position of glazes furnishing good crystals.

Group XXVII.

To this group belong all of the commercial zinc-titanic acid glazes cited in Table I. Notwithstanding the fact that these commercial glazes have an oxygen ratio of 4.0, the writers did not feel justified in enlarging the scope of these investigations by including ratios higher than 4.0. In the first place, they felt that the scope as presented, was perhaps larger than the time and facilities at hand would warrant, and would rather sacrifice breadth of scope than thoroughness in detail. In the second place, it seemed inconsistent to expect greater crystallizing tendencies in mixtures of high acid content, when all of our experience

in the production of matt glazes, which are crypto-crystalline, indicated that it was in glazes of low acid content that crystals would be easiest developed. For these reasons, the results of this group are studied with added interest.

Larger individual crystals and larger clusters were developed in this group than in the two preceding groups. In Plate XV the results are shown diagramatically. In plate XXXVIII, page 84, are shown the crystals obtained in glaze No. 2944, which has the molecular composition of

$$\left.\begin{matrix} 0.6\ ZnO \\ 0.4\ KNaO \end{matrix}\right\} \begin{cases} 0.3\ TiO_2 \\ 1.7\ SiO_2 \end{cases}$$

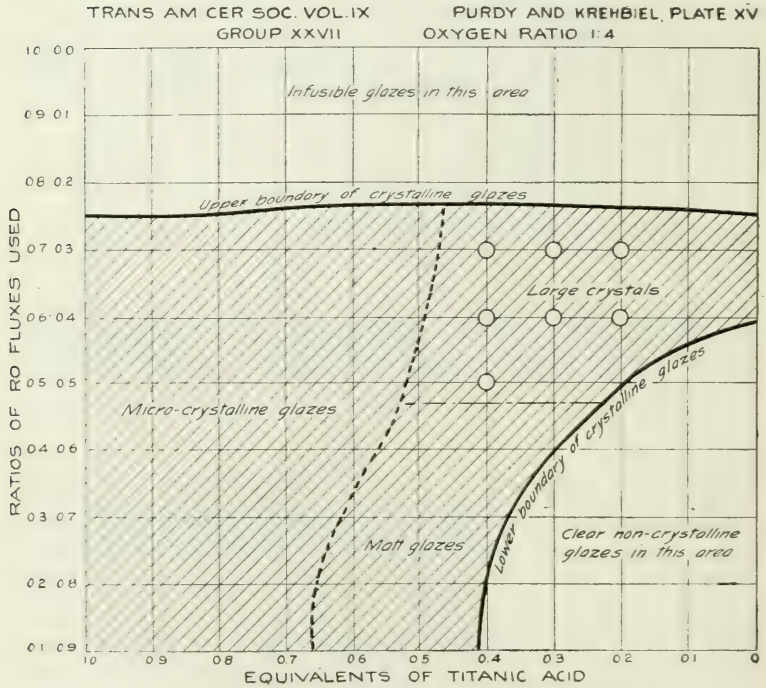


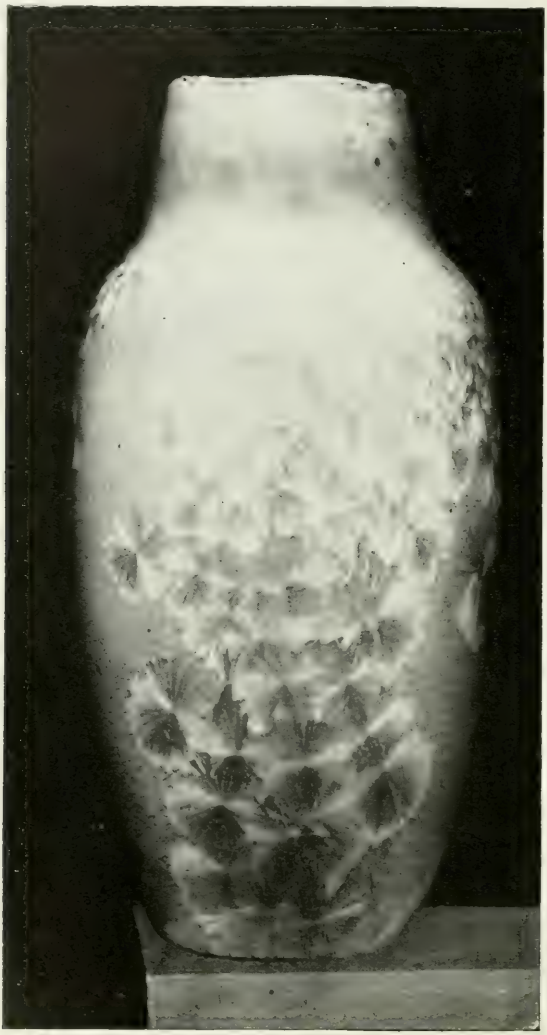
Chart showing results of crystalline glaze experiments, using zinc and alkaline as RO fluxes, and titanic acid partly replacing silica in the acid portion. Oxygen ratio of all glazes on this chart 1:4.0. Circles indicate position of glazes furnishing good crystals.



Glaze No. 346, having the formula

$$\left.\begin{matrix} 0.5\ Na_2O \\ 0.5\ ZnO \end{matrix}\right\} 1.10\ SiO_2$$

Being Glaze f, Series 2 Group IV.



Glaze No. 384, having the formula

$$\left.\begin{matrix} 0.3\ Na_2O \\ 0.7\ ZnO \end{matrix}\right\} 1.5\ SiO_2$$

Being Glaze d, Series 6, Group IV.

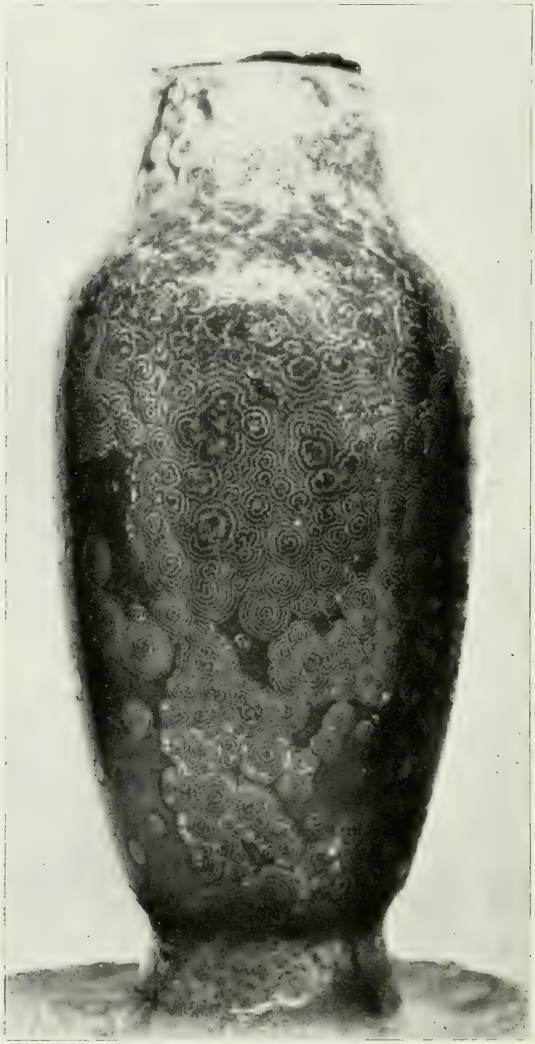
Trans. Am. Cer. Soc., Vol. IX. Purdy-Krehbiel, Plate XIX.



Glaze No. 394, having the formula

$$\left.\begin{matrix} 0.3\ Na_2O \\ 0.7\ ZnO \end{matrix}\right\} 1.6\ SiO_2$$

Being Glaze d, Series 7, Group IV.

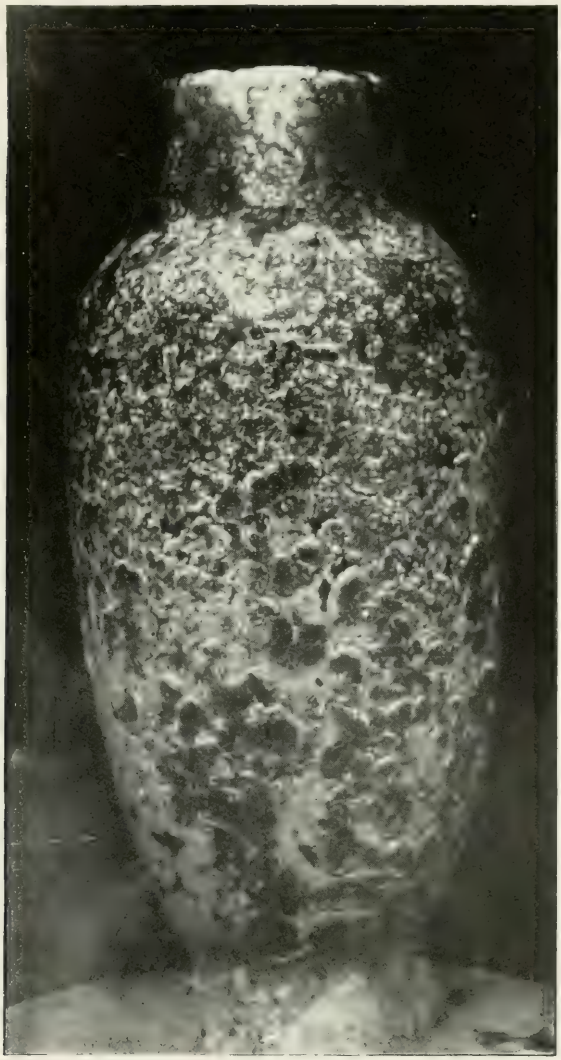


Glaze No. 1155, having the formula

$$\left.\begin{matrix} 0.4\ K_2O \\ 0.6\ MnO \end{matrix}\right\} 0.75\ SiO_2$$

Being Glaze e, Series 6, Group XI.

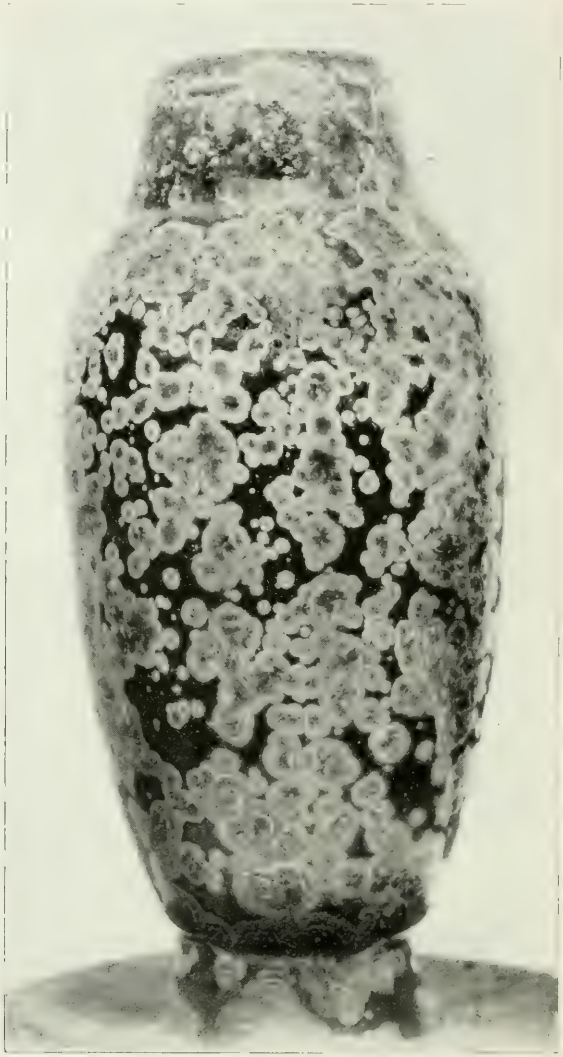
Trans. Am. Cer. Soc., Vol. IX. Purdy-Krehbiel, Plate XXI.



Glaze No. 1173, having the formula

$$\left.\begin{matrix} 0.2\ K_2O \\ 0.8\ MnO \end{matrix}\right\} 0.85\ SiO_2.$$

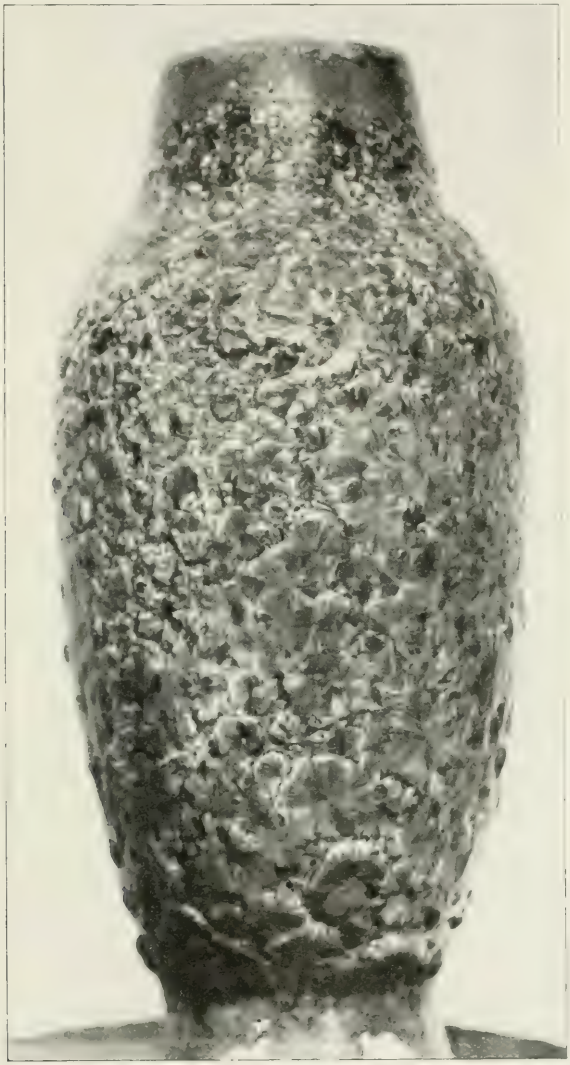
Being Glaze c, Series 8, Group XI.



Glaze No. 1235, having the formula

$$\left.\begin{matrix} 0.4\ K_2O \\ 0.6\ MnO \end{matrix}\right\} 1.20\ SiO_2$$

Being Glaze e, Series 3, Group XII.



Glaze No. 1412, having the formula

$$\left.\begin{matrix} 0.1\ Na_2O \\ 0.9\ MnO \end{matrix}\right\} 0.95\ SiO_2$$

Being Glaze b, Series 10, Group XIII.



Glaze No. 1414, having the formula

$$\left.\begin{matrix} 0.3\ Na_2O \\ 0.7\ MnO \end{matrix}\right\} 0.95\ SiO_2$$

Being Glaze d, Series 10, Group XIII.



Glaze No. 1422, having the formula

$$\left.\begin{matrix} 0.1\ Na_2O \\ 0.9\ MnO \end{matrix}\right\} .1.00\ SiO_2$$

Being Glaze b, Series II, Group XIII.



Glaze No. 1423, having the formula

$$\left.\begin{matrix} 0.2\ Na_2O \\ 0.8\ MnO \end{matrix}\right\} 1.00\ SiO_2$$

Being Glaze c, Series 11, Group XIII.



Glaze No. 1442, having the formula

$$\left.\begin{matrix} 0.1\ Na_2O \\ 0.9\ MnO \end{matrix}\right\} 1{:}10\ SiO_2$$

Being Glaze b, Series 2, Group XIV.

Trans. Am. Cer. Soc., Vol. IX. Purdy-Krehbiel, Plate XXVIII.



Glaze No. 1635, having the formula

$$\left.\begin{matrix} 0.4\ KNaO \\ 0.6\ MnO \end{matrix}\right\} 0.95\ SiO_2$$

Being Glaze e, Series 10, Group XV.



Glaze No. 2286, having the formula

$$\left.\begin{matrix} 0.50\ KNaO \\ 0.50\ ZnO \end{matrix}\right\} \left\{\begin{matrix} 0.81\ SiO_2 \\ 0.09\ TiO_2 \end{matrix}\right.$$

Being Glaze f, Series 9, Group XXI.

Trans. Am. Cer. Soc., Vol. IX. Purdy-Krehbiel, Plate XXX.

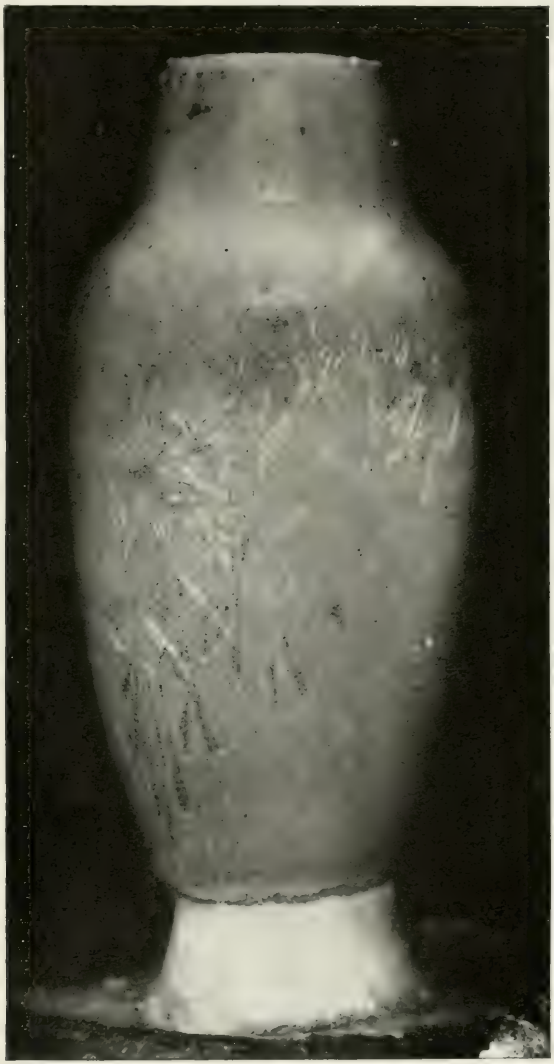


Glaze No. 2294, having the formula

$$\left.\begin{matrix} 0.3\ KNaO \\ 0.7\ ZnO \end{matrix}\right\} \left\{\begin{matrix} 0.81\ SiO_2 \\ 0.09\ TiO_2 \end{matrix}\right.$$

Being Glaze d, Series 10, Group XXI.
Blisters due to use of too much gum of tragacanth.

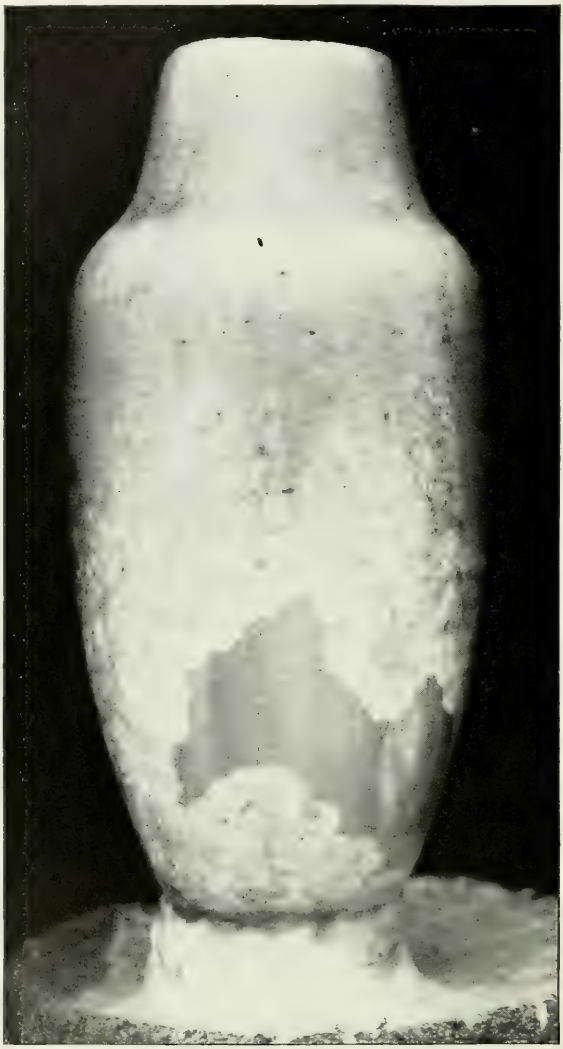
Trans. Am. Cer. Soc., Vol. IX. Purdy-Krehbiel, Plate XXXI.



Glaze No. 2306, having the formula

$$\left.\begin{matrix} 0.50\ KNaO \\ 0.50\ ZnO \end{matrix}\right\} \begin{matrix} 0.90\ SiO_2 \\ 0.00\ TiO_2 \end{matrix}$$

Being Glaze f, Series 11, Group XXI.



Glaze No. 2505, having the formula

$$\left.\begin{matrix} 0.4\ KNaO \\ 0.6\ ZnO \end{matrix}\right\} \left\{\begin{matrix} 1.0\ SiO_2 \\ 0.2\ TiO_2 \end{matrix}\right.$$

Being Glaze e, Series 9, Group XXIII.

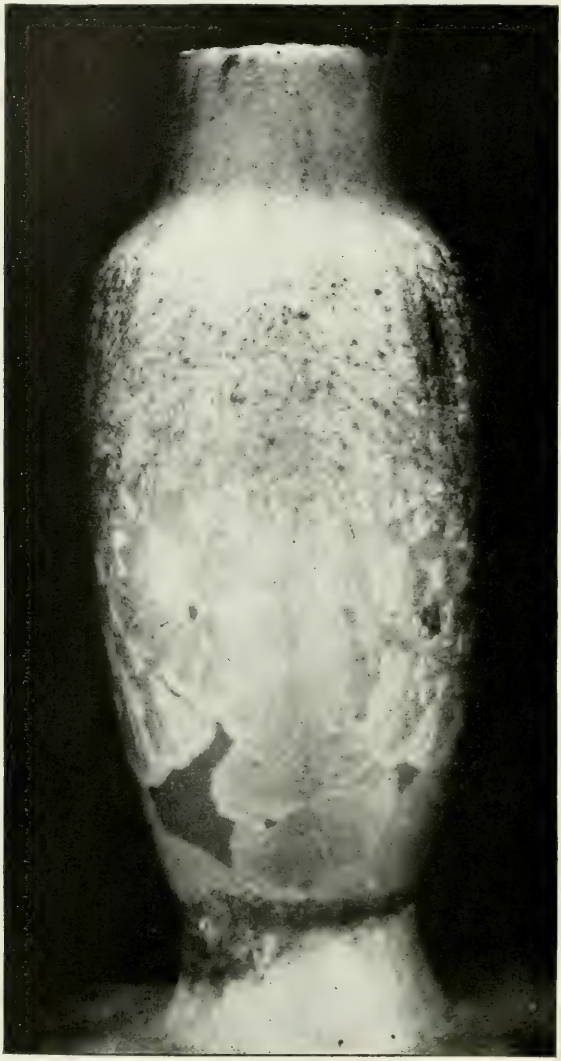
Trans. Am. Cer. Soc., Vol. IX. Purdy-Krehbiel, Plate XXXIII.



Glaze No. 2506, having the formula

$$\left.\begin{matrix} 0.5\ KNaO \\ 0.5\ ZnO \end{matrix}\right\} \left.\begin{matrix} 1.0\ SiO_2 \\ 0.2\ TiO_2 \end{matrix}\right\}$$

Being Glaze f, Series 9, Group XXIII.



Glaze No. 2515, having the formula

$$\left.\begin{matrix} 0.4\ KNaO \\ 0.6\ ZnO \end{matrix}\right\} \left.\begin{matrix} 1.10\ SiO_2 \\ 0.10\ TiO_2 \end{matrix}\right\}$$

Being Glaze e, Series 10, Group XXIII.

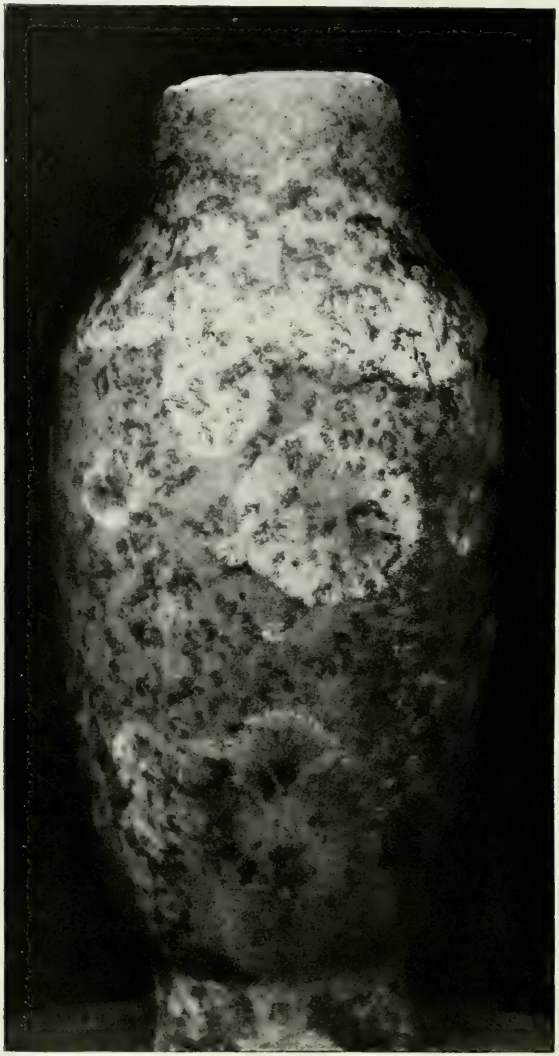
Trans. Am. Cer. Soc., Vol. IX. Purdy-Krehbiel, Plate XXXV.



Glaze No. 2516, having the formula

$$\left.\begin{matrix} 0.5\ KNaO \\ 0.5\ ZnO \end{matrix}\right\} \left.\begin{matrix} 1.10\ SiO_2 \\ 0.10\ TiO_2 \end{matrix}\right\}$$

Being Glaze f, Series 10, Group XXIII.



Glaze No. 2584, having the formula

$$\left.\begin{matrix} 0.3\ KNaO \\ 0.7\ ZnO \end{matrix}\right\} \left\{\begin{matrix} 0.9\ SiO_2 \\ 0.5\ TiO_2 \end{matrix}\right.$$

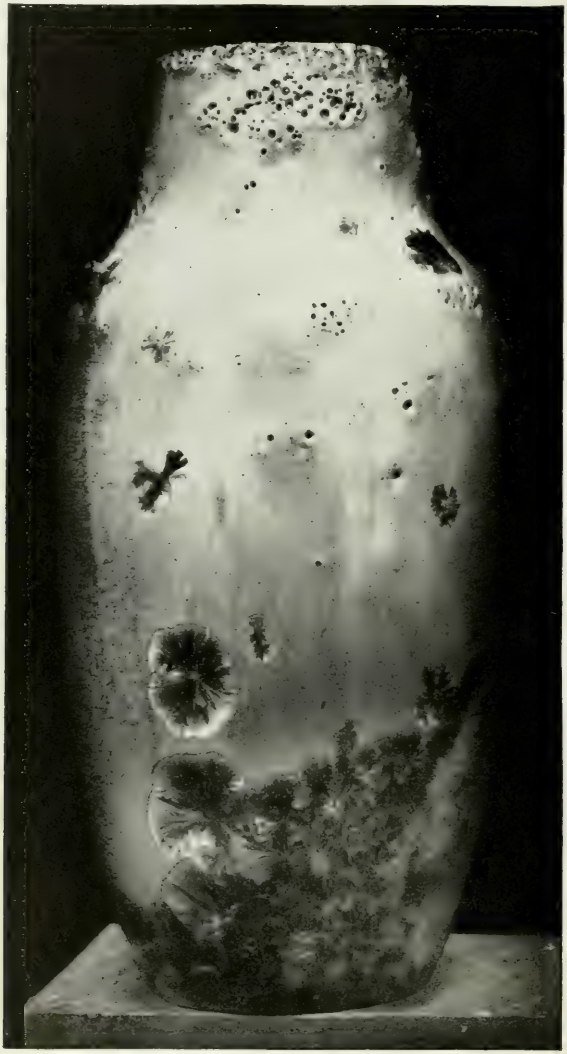
Being Glaze d, Series 6, Group XXIV.



Glaze No. 2613, having the formula

$$\left.\begin{matrix} 0.2\ KNaO \\ 0.8\ ZnO \end{matrix}\right\} \left.\begin{matrix} 1.2\ SiO_2 \\ 0.2\ TiO_2 \end{matrix}\right\}$$

Being Glaze c, Series 9, Group XXIV.



Glaze No. 2944, having the formula

$$\left.\begin{matrix} 0.3\ KNaO \\ 0.7\ ZnO \end{matrix}\right\} 1.8\ SiO_2 \left\{ 0.2\ TiO_2 \right\}$$

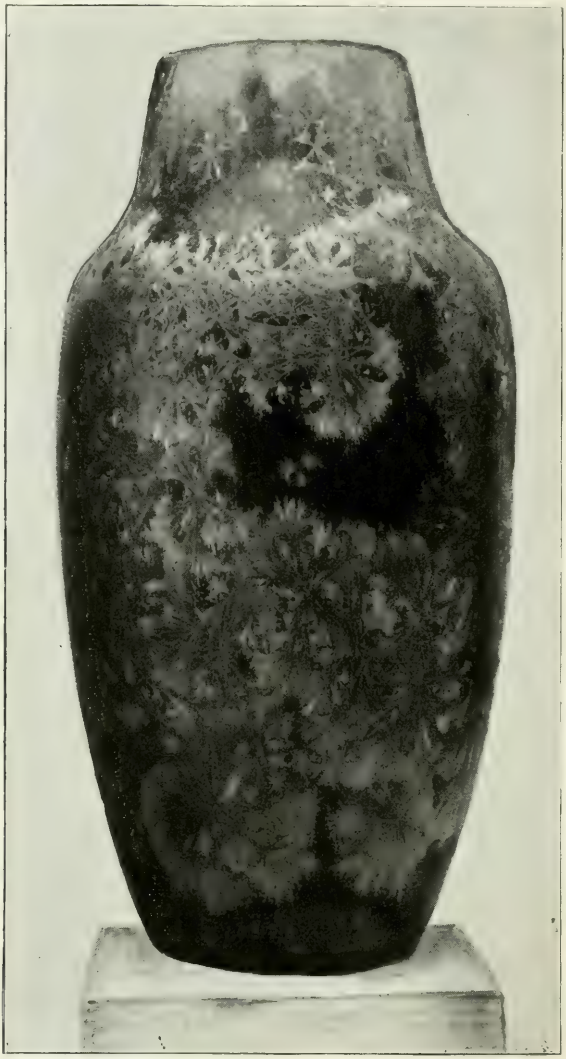
Being Glaze d, Series 9, Group XXVII.



Glaze No. 2954, having the formula

$$\left.\begin{matrix} 0.3\ KNaO \\ 0.7\ ZnO \end{matrix}\right\} 1.9\ SiO_2 \Big/ \left\{ 0.1\ TiO_2 \right.$$

Being Glaze d, Series 10, Group XXVII.



A mixed glaze having approximately the formula

$$\left.\begin{matrix} 0.33\ KNaO \\ 0.66\ ZnO \end{matrix}\right\} \left.\begin{matrix} 1.24\ SiO_2 \\ 0.29\ TiO_2 \end{matrix}\right\}$$

Summary of titanic acid groups. In Plate XVI are shown TiO_2 contents with which commercially noteworthy crystals were obtained at the various oxygen ratios. The writers are unable to explain the contour of the curve, and the possible significance of the upward trend from O.R. 3.6 to 4. is obvious.

While TiO_2 has proven to be a powerful crystallizing agent, its tendency has been toward the production of the micro, fascicular and acicular forms. In small amounts (0.4 and less) TiO_2 seems to initiate the development of crystals after the type of those formed in the ZnO, KNaO, SiO_2 matrices, but there is no evidence of its becoming a constituent part of the crystallized substance.

GENERAL CONCLUSIONS.

The result of this investigation seems to throw some light on the five questions propounded in the early portion of this article, as follows:

1st. Of the two alkalies, potash and soda, the latter in every case was the most conducive to the development of crystals. The crystals formed in the soda matrices were not only the largest, but had the most pleasing habits of growth and grouping.

2nd. The proportion of zinc and alkali most conducive to the development of crystallization in every case, save that of the glazes high in titanic acid, was,

$$\left.\begin{matrix} 0.3\ ZnO \\ 0.7\ KNaO \end{matrix}\right\} \text{ to } \left\{\begin{matrix} 0.6\ ZnO \\ 0.4\ KnaO \end{matrix}\right.$$

3rd. Manganese oxide had by far the greatest crystallizing tendency, producing not only large crystals but also crystals of surprisingly varied habits of growth. Zinc oxide had a tendency to produce large crystals in local areas, as though the crystallizing substance had seggregated. Titanic acid, on the other hand, produced crystals that were small but evenly distributed throughout the mass.

4th. The character and shape of crystals induced by

TABLE V. Molecular and Batch Proportions of Experimental Glasses.

Name of Ingredient	Number 1		Number 2		Number 3		Number 4		Number 5		Number 6		Number 7		Number 8	
	Molecules	Per Cents.	Molecules	Per Cents.	Molecules	Per Cents.	Molecules	Per Cents	Molecules	Per Cents.	Molecules	Per Cents	Molecules	Per Cents.	Molecules	Per Cents.
Silica	2	50 4	3	60.4	4	67 4	5	71.8	6	75 3	3	50.0	4	57.1	5	62 4
Lime	1	23.6	1	18 8	1	15 6	1	13.4	1	11 7	1	15.6	1	13.3	1	12.6
Soda	1	26.0	1	20.8	1	17 4	1	14.8	1	13 0	2	34 4	2	29 6	2	26.0

1. Completely devitrified on slow cooling.
2. Chiefly devitrified on slow cooling
3. But little devitrified.
4. Good glass.
5. Melted only with difficulty.
6. Half devitrified.
7. Good glass.
8. Good glass.

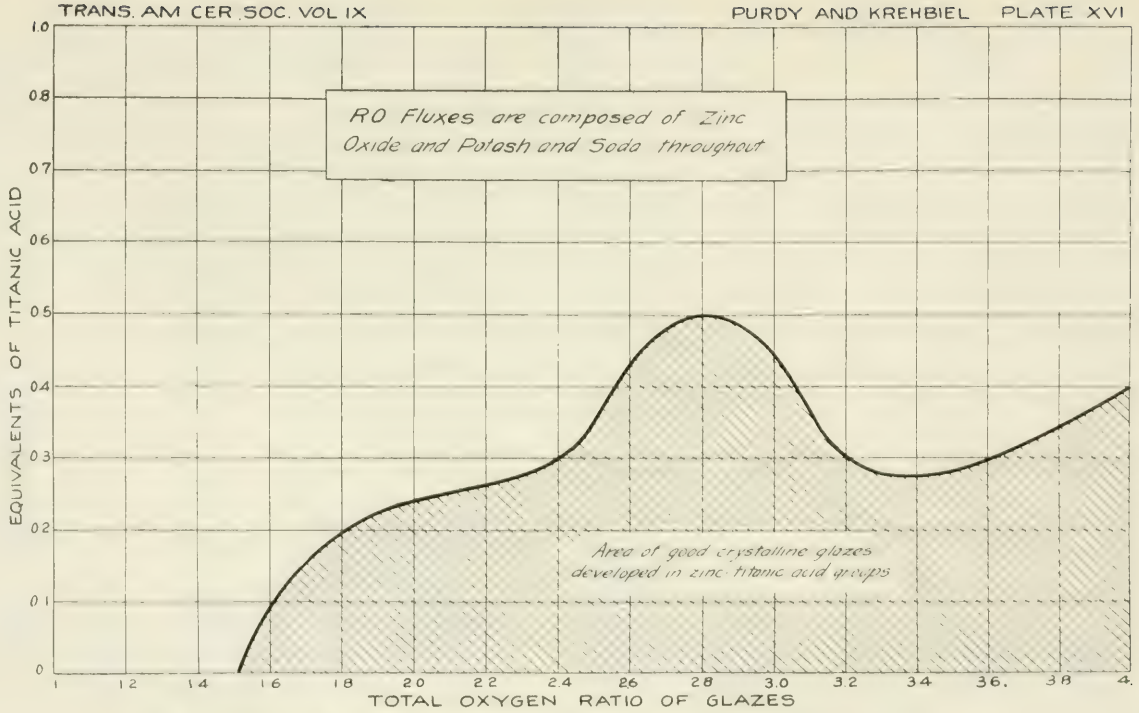


Chart summarizing the results of the various series of zinc-titanic acid glazes.

TABLE VI. Resume of Facts noted in Titanic Acid Groups.

Group No.	Oxygen Ratio	Range in KNaO Eqv. between Fusible and soluble areas	Character and habits of crystalline growth.	Number of glazes in which commercially attractive crystals were developed.	Range in molecular constitution within which most promising results were obtained			
					ZnO Eqv	KNaO Eqv.	TiO_2 Eqv.	SiO_2 Eqv.
XVII	1.0	Practically none	Micro crystalline, porphyritic	none				
XIX	1.4	0.4—to 0.44	Larger and fewer than in XVII. Small radial clusters on shoulders of vases, fascicular on vertical faces.	none	0 6	0 4	0.21-0.49	0.21-0.49
XXI	1.8	0.3—0.8	Fascicular on vertical and radial on horizontal faces.	9	0.4—0.7	0.3—0.6	0—0.63	0.27-0.90
XXIII	2.4	0.3—0.7	Larger and fewer than in preceding groups and changed from fascicular to clusters.	10	0.4 0.6	0.4—0.6	0—0.50	0.7—1.2
XXIV	2.8	None soluble. 0 0.2 KNaO infusible range	Still larger clusters. Most consistent when ZnO=0.8 Eqv.	13	0.2—0.7	0.3—0.8	0—0.50	0.9—1.4
XXV	3.2	None soluble. 0—0.3 KNaO infusible range	Micro-crystalline area smaller than in XXIV. Acicular crystals on vase between TiO_2 content of 0.4-0.7 inclusive. With 0.3 eqv. of TiO_2 and less, the crystals are commerically attractive.	6	0.1—0.7	0.3—0.9	0—0.70	0.9—1.6
XXVI	3.6		Similar to group XXV	3	0.3—0.5			
XXVII	4.0	None soluble 0—0.2 KNaO infusible range	Area of commercially note worthy glazes developed is larger than those in XXV and XXVI but not equal to those of XXIII and XXIV	7	0.2—0.7	0.3—0.8	0—0.40	1.6—2.0

manganese can not be adequately described. The globular growths, that under a magnifying glass were handsome, produced *en mass* an effect that was anything but pleasing. The concentric growth, with the delicate spiral lines in lighter tints, were superb, and the later crystals producing variegated fawn-colored effects were very beautiful.

5th. The limits of oxygen ratio permissible in the crystalline glazes were not established. The results, however, do seem to warrant the statement that an oxygen ratio of 1 : 2.8 is better suited to the development of crystals than that of 1 : 4 as used in practice today.

Schott[1] found similar conditions in his study of the Jena glass, are shown in Table No. V, on page 88.

A study of these results confirms our findings in that Schott's glasses also crystallized more freely at oxygen ratios well below 1 : 4, and also that glasses in which the RO is composed of 1 soda to 1 lime crystallize more freely than those in which the soda is increased at the expense of the alkaline earth.

DISCUSSION.

The Chair: I would like to ask whether, after getting these results, an attempt was made to reproduce any of them using the same firing conditions and the same glaze compositions.

Mr. Purdy: Yes, and we found considerable trouble in getting consistent results in different burns. In a few cases, we secured duplicate results. We generally purposely varied the heat treatment, so as to produce in one case a clear gloss; in another, large crystals, and in another, a perfectly matt surface.

The Chair: Was that variation in the heat treatment, or in the glaze mixture?

Mr. Purdy: The variation was in the method of cooling, in all cases. This is described in the paper, but in my anxiety not to burden you by reading the entire paper, I

[1]Wagner, Chemical Technology, Crooke's Translation, p. 594.

gave this rather incomplete synopsis, off-hand. In that way, I omitted to mention many points which should be brought out in a proper discussion of the subject.

The Chair: If there is to be a commercial future for this type of glaze, it must be shown to be in a measure under control.

Mr. Purdy: That is a subject which will be taken up at the University of Illinois the next semester. We have covered the field in this hurried way, and now, selecting the better crystalline glazes, we are going to try different heat treatments and see if they will remain constant.

The Chair: When you get the crystalline formation under varying heat treatments, are the crystals always the same, i. e. of the same order?

Mr. Purdy: Yes, sir.

Mr. Gates: And always different. In other words, when you get one, you know you will never get another just like it, for the performance is so different under different cooling conditions. The liquid consistency must be just right, and just as long as it is right the crystals will continue to grow, their lines of crystallization shooting or growing outward from each crystal center until the one touches the other and the whole surface is covered. I also think the density of the liquid has to do with the fineness of the crystallization.

A very interesting study on this subject is to take the old experiment of mixing stale beer and sulphate of magnesium and applying to glass. As the mixture dries or whenever it dries to the proper consistency, crystallization will commence, and as the lines of this crystallization extend out, if new liquid is carefully fed on,—just ahead of the lines of crystallization—they can be continued in their growth until they become enormous. This I think interesting as showing that they do grow, although of course impossible to duplicate in a glaze. Still I think the same principle applies in that the glaze must reach the proper fluidity—neither too great or too little—and must be held right there during the crystallizing period.

The Chair: Are these differences merely a question of size?

Mr. Gates: No. There is a difference of arrangement of the crystals in groups, etc.

The Chair: I have heard of crystals being described as cannibals; that is, as the process of crystallization goes on, the big crystals eat the little crystals, just as big fish eat the little ones.

Mr. Purdy: A constancy of result is found in all of the titanic acid groups, the needle-like crystals all being in the same areas of the curve sheets, and inasmuch as it required two burns to cover each group, we think the uniformity of results there speaks well for a possible uniformity in the development of crystals from burn to burn. We did not have the same uniformity where zinc was used alone, but with zinc and titanium used together, we have greater uniformity.

Mr. Stover: Did you try to make a series, using lime as the crystallizing oxide?

Mr. Purdy: No.

Mr. Stover: The reason that I ask is that I got one of the most beautiful crystalline effects that I ever saw, when firing a piece of cement rock, from up near Phillipsburg. A party sent down a piece of the rock, which I put in the kiln, firing it to about cone ten, or just about enough to melt it, and it produced beautiful crystals. It was thought to be a rock whose composition agrees pretty closely with the formula used in making Portland cement.

Mr. Purdy: Perhaps it was not sufficiently emphasized in those parts of the paper which I read, but many of these glazes that crystallized best, were of the same composition as ordinary glass, except that in the place of lime we used oxide of zinc; and in other places, instead of all the acid components being silica, we used some titanic acid. It is interesting to know that the glazes which behaved best on the ware, were very similar in composition and crystallizing tendencies to ordinary glass.